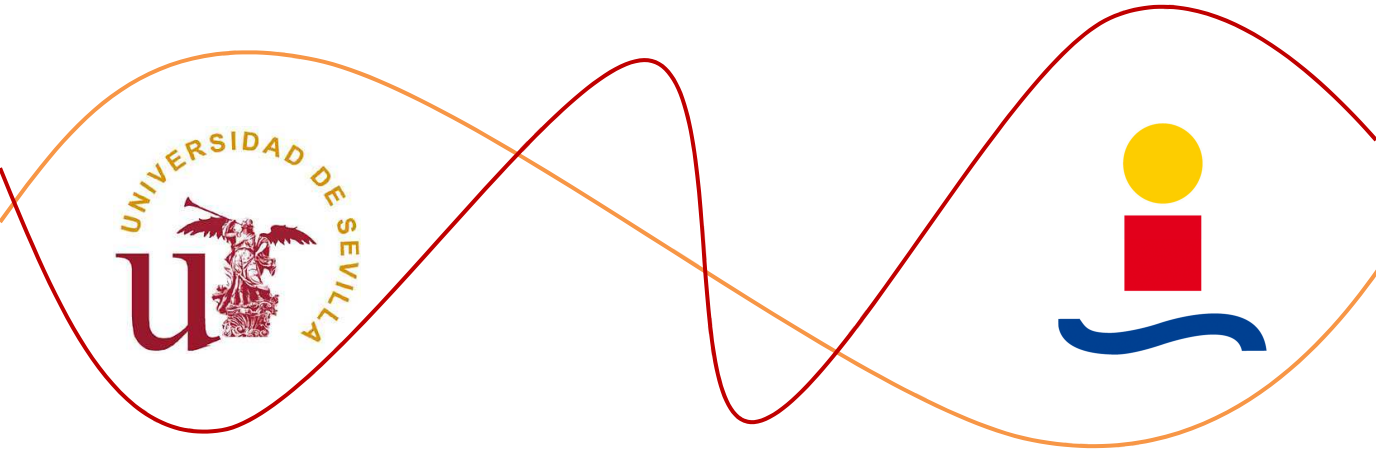


Studies on tar formation and conversion for the development of a three-stage gasifier

Estudio de la reactividad en fase gas y sobre lecho de carbonizado del alquitrán generado durante la devolatilización de biomasa y residuos

DIEGO J. FUENTES CANO

Tesis doctoral presentada para optar al título de Doctor por la

Universidad de Sevilla

(Doctoral thesis for the degree of Doctor of Philosophy)

Estudio de la reactividad en fase gas y sobre lecho de carbonizado del alquitrán generado durante la devolatilización de biomasa y residuos

(Studies on tar formation and conversion for the development of a three-stage gasifier)

Diego J. Fuentes Cano

Director de Tesis: Dr. Alberto Gómez Barea

Departamento de Ingeniería Química y Ambiental
Escuela Superior de Ingenieros (Universidad de Sevilla)
Abril 2013

A Javi, a Mayi y a Clara

A Marina

Resumen

La gasificación autotérmica de biomasa y residuos en lecho fluido para generación eléctrica distribuida presenta notables ventajas respecto a otras opciones. No obstante esta tecnología presenta ciertas limitaciones que frenan su implantación comercial: la limitada conversión del combustible, debida a la incompleta conversión del carbonizado, y la elevada temperatura de condensación del gas, causada por la alta concentración de alquitranes pesados en éste. Las medidas que se han desarrollado para hacer frente a ambos problemas se basan en métodos complejos o caros, haciendo inviable la implantación de esta tecnología en sistemas de pequeña o mediana escala. El Grupo de Bioenergía de la Universidad de Sevilla está desarrollando una nueva tecnología (FLETGAS) que persigue el objetivo de obtener un gas combustible a partir de biomasas y residuos apto para ser quemado en motores de gas. El sistema se basa en tres etapas: gasificación en lecho fluido a baja temperatura (700-800°C), reformado con vapor a alta temperatura (1200°C) y filtración en un lecho móvil de carbonizado. La presente tesis estudia la formación y conversión de alquitranes e hidrocarburos ligeros en las diferentes etapas del nuevo gasificador con objeto de determinar las condiciones de funcionamiento que permitan reducir la concentración de alquitranes pesados en el gas producto y, por tanto, producir un gas con un punto de rocío suficientemente bajo para ser quemado en un motor.

En la primera parte de la tesis (Capítulos 3 y 4) se estudia la influencia de las condiciones de operación sobre los productos de la devolatilización de lodos secos de depuradora (DSS) en un lecho fluido de laboratorio. Se ha determinado el efecto de la temperatura y la del vapor sobre la composición de alquitrán, estableciéndose los principales mecanismos de conversión durante la generación primaria de volátiles (en el lecho denso) y secundaria (freeboard). Se ha estudiado también el efecto de la operación con dos temperaturas diferentes en el reactor (lecho denso y freeboard), demostrando que este modo de operación influye decisivamente en la composición de los volátiles. Por el contrario, a temperaturas inferiores a 900°C, el vapor afecta muy poco a la cantidad y naturaleza de los alquitranes generados. Se han obtenido correlaciones entre hidrocarburos ligeros y alquitranes que sirven para estimar de forma rápida el punto de rocío del gas.

En la segunda parte de la tesis (Capítulo 5) se ha investigado la conversión de alquitranes aromáticos (naftaleno y tolueno) sobre varios lechos de carbonizado en un reactor de lecho fijo de laboratorio. Los resultados experimentales han demostrado que el lecho de carbonizado reduce eficazmente la concentración de alquitrán. A temperaturas superiores a 850°C, tiempos de residencia de 0,3 s y concentraciones de vapor de más del 15 vol% se alcanzan conversiones casi completas de los alquitranes analizados. Se han obtenido expresiones cinéticas para la conversión de alquitrán sobre los diferentes carbonizados teniendo en cuenta su desactivación. Se ha utilizado la cinética obtenida para simular el proceso FLETGAS corroborando trabajos anteriores (Nilsson et al., 2012) donde se demostraba que la tercera etapa del nuevo gasificador sería capaz de convertir el alquitrán pesado hasta los niveles necesarios para generar un gas de salida con el punto de rocío deseado.

Abstract

Autothermal air-blown gasification in a fluidized bed gasifier (FBG) is a promising alternative for the valorization of biomass and waste for medium scale plants. However this gasification procedure presents two limitations: the incomplete fuel conversion and the high dew point of the gas caused by the high concentration of heavy tars in it. Measures have been developed to overcome these limitations, but the increase in the costs prevents their use for power production in medium-scale processes. Aiming at overcoming the inherent limitations of conventional FBG, a new three-stage gasification technology (FLETGAS process) is under development by the Bioenergy Group at the University of Seville. The three stages comprises: 1- FB gasification at low temperature (700-800°C), 2- oxidation/reforming of the gas at high temperature (1200°C maximum) and 3- catalytic filtration in a char moving bed. The present thesis deals with the formation and conversion of tars and light hydrocarbons within the different stages of the new gasifier with the objective of determining the operating conditions for the reduction of the concentration of heavy tars in the gas and thus, to produce a gas with a dew point low enough to be burnt in a gas engine.

The first part of the thesis (Chapters 3 and 4) deals with the influence of operating conditions over the composition of volatiles produced during dried sewage sludge (DSS) devolatilization of in an FB. The effects of the temperature, steam concentration and thermal division of the reactor (dense bed and freeboard) on composition of tars and hydrocarbons during both primary generation (dense bed) and subsequent conversion of these along the gasifier (freeboard) have been investigated. The results allow understanding of the main conversion mechanisms taking place in the gasifier, demonstrating that the achievement of two thermal zones in the reactor has a significant influence on tar and light hydrocarbons composition of the gas produced during devolatilization, whereas the steam in the fluidization agent hardly affect tar composition up to 900°C. The results have been used for the establishment of operation conditions in the first stage of the FLETGAS gasifier.

The second part of the thesis (Chapter 5) investigates the conversion of model aromatic tars (naphthalene and toluene) over various chars in a laboratory fixed bed reactor. The experimental results have demonstrated that the char bed effectively reduces the tar concentration. Almost complete conversion has been measured at temperatures above 850°C, residence time of 0.3 s and steam concentration above 15 vol%. Empirical kinetic expressions for tar conversion over the different chars have been obtained accounting for char deactivation. The use of this kinetics for simulating the FLETGAS process has demonstrated that the third stage of the new gasifier is able to convert the heavy tars to the extent necessary for the production of gas with the desired dew point. This work establishes the experimental conditions (temperature, gas residence time and steam concentration) necessary to maintain high enough the rate of tar conversion over the char bed, i.e. minimizing the deactivation.

Papers

This thesis is based on a number of papers already published or submitted to journals and international conferences. They are the following:

PAPER 1. Fuentes-Cano, D.; Gómez-Barea, A.; Nilsson, S.; Ollero, P. The influence of temperature and steam on the yields of tar and light hydrocarbon compounds during devolatilization of dried sewage sludge in a fluidized bed. Fuel, 2013; 108, 341.

PAPER 2. Fuentes-Cano, D.; Gómez-Barea, A.; Nilsson, S. Generation and secondary conversion of volatiles during devolatilization of dried sewage sludge in a fluidized bed. Ind. Eng. Chem. Res., 2013; 52, 1234.

PAPER 3. Fuentes-Cano, D.; Gómez-Barea, A.; Nilsson, S.; Ollero, P. Decomposition kinetics of model tar compounds over chars with different internal structure to model hot tar removal in biomass gasification. Chem. Eng. J. (accepted for publication).

PAPER 4. Gómez-Barea, A.; Leckner, B.; Villanueva-Perales, A.; Nilsson, S.; Fuentes-Cano, D. Improving the performance of fluidized bed biomass/waste gasifiers for distributed electricity: A new three-stage gasification system. Appl. Ther. Eng., 2012; 50, 1453.

PAPER 5. Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D.; Ollero, P. Gasification of biomass and waste in a staged fluidized bed gasifier: modeling and comparison with one stage units. Fuel, 2012; 97, 730.

PAPER 6. Fuentes-Cano, D.; Gómez-Barea, A.; Nilsson, S.; Campoy, M.; Ollero, P. The effect of temperature and steam concentration on the yields of tar compounds in fluidized bed pyrolysis. Proc. of 19th European Biomass Conference, June 2011, Berlin (Germany).

The author of the present thesis has participated in other publications submitted to international conferences and journals, which partially overlap with the topic of the thesis, but which are not considered direct publication from this work. These papers are listed below.

PAPER 7. Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D. Gasification reactivity of char from dried sewage sludge in a fluidized bed. Fuel, 2012; 92, 346.

PAPER 8. Campoy, M.; Gómez-Barea, A.; Fuentes-Cano, D.; Ollero, P. Tar reduction by primary measures in an autothermal air-blown fluidized bed biomass gasifier. Ind. Eng. Chem. Res., 2010; 49, 11294.

PAPER 9. Fuentes-Cano, D.; Claro, G.; Nilsson, S.; Gómez-Barea, A.; Ollero, P. Investigation of tar properties for tar removal by scrubbing. Proc. of 18th European Biomass Conference, May 2010, Lyon (France).

PAPER 10. Gómez-Barea, A.; Campoy, M.; Nilsson, S.; Fuentes-Cano, D.; Plumed, M.J.; Villanueva, A.; Ollero, P. Valorisation of dried sewage sludge via gasification in fluidised bed. Proc. of 16th European Biomass Conference, June 2008, Valencia (Spain).

PAPER 11. Campoy, M.; Gómez-Barea, A.; Fuentes-Cano, D.; Nilsson, S.; Ollero, P. Techno-economical analysis for the revamping of an air-blown fluidised bed biomass gasification plant by using enriched air and steam. Proc. of 17th European Biomass Conference, June 2009, Hamburg (Germany).

PAPER 12. Gómez-Barea, A.; Fuentes-Cano, D.; Nilsson, S.; Tirado, J.; Ollero, P. Fluid-dynamics of a cold model of a fluidized bed gasification system with reduced tar content. Proc. of 18th European Biomass Conference, May 2010, Lyon (France).

PAPER 13. Campoy, M.; Gómez-Barea, A.; Ollero, P.; Nilsson, S.; Fuentes-Cano, D. Gasification of wastes in a pilot fluidized bed gasifier. Proc. of 19th European Biomass Conference, June 2011, Berlin (Germany).

PAPER 14. Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D.; Peña, Y.; Ollero, P.; Campoy, M. Devolatilization of two agricultural residues in fluidized bed: product distribution and influence of fluidization agent. Proc. of 19th European Biomass Conference, June 2011, Berlin (Germany).

PAPER 15. Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D.; Ollero, P. Three-stage gasification system for producing a gas with low tar content: concept and modeling. Proc. of 19th European Biomass Conference, June 2011, Berlin (Germany).

During the thesis the author of this thesis has been granted by the following two projects:

- Desarrollo de una tecnología de gasificación de biomasa basada en un gasificador flexible de tres etapas
  Proyecto de Excelencia de la Junta de Andalucía. TEP-03893. **2009-2012**
  Main researcher: Pedro Ollero de Castro

- Estudio de la conversión térmica mediante inyección de aire secundario para la eliminación de alquitranes en gasificadores de lecho fluido y valoración técnico-económica respecto de otras rutas (TC2GAS).
  Proyecto Plan Nacional I+D+I. ref: ENE2005-08828. **2005–2008**
  Main researcher: Alberto Gómez Barea

Additionally, the student has participated in specific tasks in the following projects during his collaboration in the Department of Chemical and Environmental Engineering.

- Oxicombustión y oxigasificación el lecho fluidizado: estudio de la conversión de carbonizado para el diseño y optimización de equipos de captura de segunda generación
  Plan Nacional. ENE2012-37999. **2012-2015.**
  Main researcher: Alberto Gómez Barea

- Biorefinerías Sostenibles
  Contrato 68/83 (CENIT Project) **2010–2013** (Company: *Abengoa New technologies*)
  Main researcher: Pedro Ollero de Castro

- GASIFICADOR Fase II
  Contrato 68/83 (PI-0804/2011) **2010-2011.** (Company : *CIUDEN and INERCO*)
  Main researcher: Alberto Gómez Barea

- Generación distribuida de electricidad a partir de gasificación de biomasa en lecho fluidizado.
  Contrato 68/83, ref: PI-0261/08, **2008–2010** (Company: *Inerco*)
  Main researcher: Pedro Ollero de Castro

- Gasificación de fracciones orgánicas procedentes de residuos sólidos urbanos.
  Contrato 68/83, ref: PI-0476/2008, **2008–2009** (Company: *Inerco, Aborgase*)
  Main researcher: Pedro Ollero de Castro

- Proyecto de investigación para evaluar la eficacia del proceso de gasificación de lodos y su aplicabilidad en el canal de Isabel II
  Contrato 68/83, ref: PI-0550/2008, **2007–2008** (Company: *Canal Isabel II*)
  Main researcher: Pedro Ollero de Castro

- Gasificador de biomasa para el empleo asociado a calderas de combustible fósil.
  Contrato 68/83, Ref: PI-0091/2005, **2005–2008** (Company: *Inerco*)
  Main researcher: Pedro Ollero de Castro

Content

Agradecimientos

Quiero dar las gracias a todos aquellos que me han apoyado, ayudado y alentado durante la realización de esta tesis.

En primer lugar quiero agradecerle a mi director, Alberto, toda la ayuda y los consejos recibidos así como la oportunidad de realizar este trabajo. Su incansable deseo de saber y su visión pragmática de la investigación han guiado, desde el comienzo, el trabajo que aquí se presenta.

Igualmente quiero agradecer a Pedro Ollero la oportunidad de formar parte del Grupo de Bioenergía de la Universidad de Sevilla del cual es director e investigador principal.

Quiero agradecer muy especialmente a mi compañera Susanna Nilsson su ayuda con las simulaciones incluidas en la tesis y a mi compañero Israel Pardo su dedicación durante los laboriosos análisis de alquitranes que supusieron un largo verano perdido en los laboratorios.

Asimismo me gustaría expresar mi agradecimiento a todos los miembros del Departamento de Ingeniería Química y Ambiental por la colaboración y el apoyo prestado durante estos años. A mi colega Manolo por su ayuda siempre oportuna; a Verónica y Elisa por el trabajo experimental realizado y a Carlos y Celia por los cuidadosos análisis porosimétricos realizados.

Igualmente quiero agradecer a mi familia no solo su ánimo e interés en estos últimos años sino el esfuerzo que me han dedicado durante toda una vida.

Y por último quiero agradecerte, Marina, todo el amor y la comprensión que me han permitido seguir adelante.

Resumen de la tesis doctoral

1. Introducción

El incremento de la demanda energética mundial, el progresivo agotamiento de los yacimientos de combustibles fósiles y la creciente preocupación por el deterioro ambiental debido al uso de dichos combustibles impulsan la búsqueda de nuevas fuentes de energía limpias y renovables. La valorización de biomasa (madera sin tratar, residuos forestales, residuos de la agricultura, etc…) o residuos (lodos de depuradora, residuos sólidos urbanos, residuos industriales, etc…) para la producción de electricidad y productos químicos es una alternativa interesante para la reducción de la dependencia de combustibles fósiles.

Uno de los procesos más prometedores para la producción energética a partir de biomasa y residuos es la gasificación. Este proceso permite obtener a partir de un combustible sólido un gas que contiene la mayor parte de la energía del combustible original en forma química. En su versión estándar el proceso consiste en una oxidación parcial del combustible que se consigue añadiendo una cantidad sub-estequiométrica de agente oxidante (generalmente aire) al sistema. Las reacciones de oxidación aportan el calor necesario para mantener el reactor a una temperatura suficiente para producir la descomposición térmica del combustible.

Los diseños de gasificadores se basan en tres tipos fundamentales: gasificadores de lecho fijo-móvil, de lecho fluido y de lecho arrastrado. Los diseños basados en un lecho fijo se dividen en gasificadores en co-corriente y en contra-corriente refiriéndose al sentido relativo de los flujos de combustible sólido y gas. En el caso de los diseños en co-corriente la conversión de alquitranes es elevada pero no se alcanza conversión completa del combustible (presencia de carbono (char) en el residuo sólido) mientras que los sistemas en contra corriente alcanzan una elevada conversión del char con el inconveniente de producir un gas con una elevada concentración de alquitranes. Por problemas asociados al escalado el tamaño máximo de estos reactores está limitado a unos pocos MW. Por el contrario los gasificadores de lecho arrastrado, pese a producir un gas sin alquitranes y con elevada conversión de carbono, sólo son económicamente viables a grandes escalas.

De entre los diferentes tipos de gasificadores los que operan en lecho fluido son los que presentan mejores características para producción de energía eléctrica distribuida a partir de biomasa para pequeña y mediana escala. Estos gasificadores son fácilmente escalables, aceptan variaciones en la calidad del combustible y proporcionan elevadas velocidades de conversión del combustible. Sin embargo los diseños convencionales en lecho fluido (aquellos con una única etapa y alimentados con aire) presentan importantes inconvenientes que afectan principalmente a la limpieza del gas producto y a la eficiencia en la conversión del combustible. La presencia de alquitranes (hidrocarburos de alto peso molecular) en el gas producto limita el uso final del gas a procesos en los que no sea necesario un enfriamiento previo de la corriente gaseosa como su combustión directa en una caldera. Para otro tipo de usos son necesarias costosas etapas de acondicionamiento y limpieza del gas que hacen económicamente inviables las instalaciones de pequeña y media potencia. El principal problema asociado a la presencia de alquitranes en el gas producto es que, mientras que a alta temperatura permanecen en estado gaseoso, cuando el gas es enfriado comienzan a condensar provocando la obstrucción de las conducciones y el deterioro de equipos debido a su elevada corrosividad.

Tanto la elevada presencia de alquitranes en el gas como la baja conversión del combustible se deben a que la temperatura de los gasificadores en lecho fluido no es suficientemente alta (700-900°C). Mayores temperaturas mejorarían estas dos limitaciones pero aumentarían el riesgo de formación de sinterizados en el lecho. Con objeto de reducir la presencia de alquitranes en el gas producto las posibles medidas que pueden aplicarse se dividen en primarias (aquellas efectuadas dentro del propio sistema de gasificación) y secundarias (basadas en equipos auxiliares aguas abajo del gasificador). Las medidas secundarias pese a haberse demostrado eficaces en la eliminación de alquitranes de la corriente gaseosa implican elevados costes de implantación y operación lo cual limita su uso.

Las medidas primarias para la conversión de alquitranes incluyen la modificación de las condiciones de operación del gasificador, la adición de aditivos-catalizadores al lecho y la modificación del diseño del gasificador. Para un gasificador convencional en lecho fluido estas medidas incluyen la modificación de la temperatura de operación, la adición de vapor, la estratificación del agente oxidante y la adición de catalizadores al lecho. El incremento de la temperatura del sistema se consigue aumentando la relación oxidante/combustible, sin embargo dado que la temperatura máxima está limitada por los problemas de aglomeración del lecho no es posible alcanzar la conversión completa de alquitrán o del carbonizado. Además el aumento de temperatura lleva aparejado la formación de compuestos aromáticos de elevado peso molecular que condensan a elevada temperatura incluso a muy baja concentración. La adición de vapor mejora la conversión del carbonizado y reforma parcialmente el alquitrán generado; sin embargo la reducción en la producción de alquitrán está lejos de ser suficiente para la combustión directa del gas en un motor. Además, si se aporta vapor (típicamente a temperaturas de entre 200 y 400°C), es necesaria una mayor adición de oxígeno (aire) para mantener el nivel térmico del reactor. La estratificación de oxidante, al igual que el aumento de la proporción de aire, reduce la cantidad total de alquitrán en el gas producto a costa de aumentar el peso molecular de los mismos. Por último la adición de ciertos catalizadores minerales (olivino, dolomita o cal) al

lecho fluido ha demostrado reducir considerablemente la cantidad de alquitranes en el gas aunque la disminución del punto de rocío de éstos es insuficiente. El char producido tras la devolatilización ha demostrado ser un material capaz de convertir el alquitrán a velocidades similares a otros catalizadores comerciales. Sin embargo, al igual que para los otros materiales, el bajo tiempo de contacto entre el gas y el sólido en un lecho fluido es insuficiente para alcanzar una conversión alta de alquitrán.

Por lo tanto, la optimización de sistemas convencionales de gasificación en lecho fluidizado no permite alcanzar los niveles de limpieza del gas necesarios para su uso directo en motores de gas para producción eléctrica. Sin embargo el conocimiento que se ha generado durante el estudio de las citadas medidas sobre la conversión de los alquitranes y del carbono del combustible es de utilidad para el diseño y operación de nuevos sistemas de gasificación que permitan superar las limitaciones de los sistemas convencionales.

Con este objetivo, en el Departamento de Ingeniería Química y Ambiental se está desarrollado un nuevo diseño de gasificador en tres etapas donde, mediante la estratificación del agente gasificante y la mejora del contacto entre los compuestos gaseosos y el carbonizado sólido, se alcance el doble objetivo de eliminar la presencia de alquitranes pesados en el gas producto e incrementar la conversión global del combustible. La Fig. R-1 presenta un esquema conceptual del proceso donde se muestran las corrientes de gas y sólidos en las distintas zonas del gasificador.

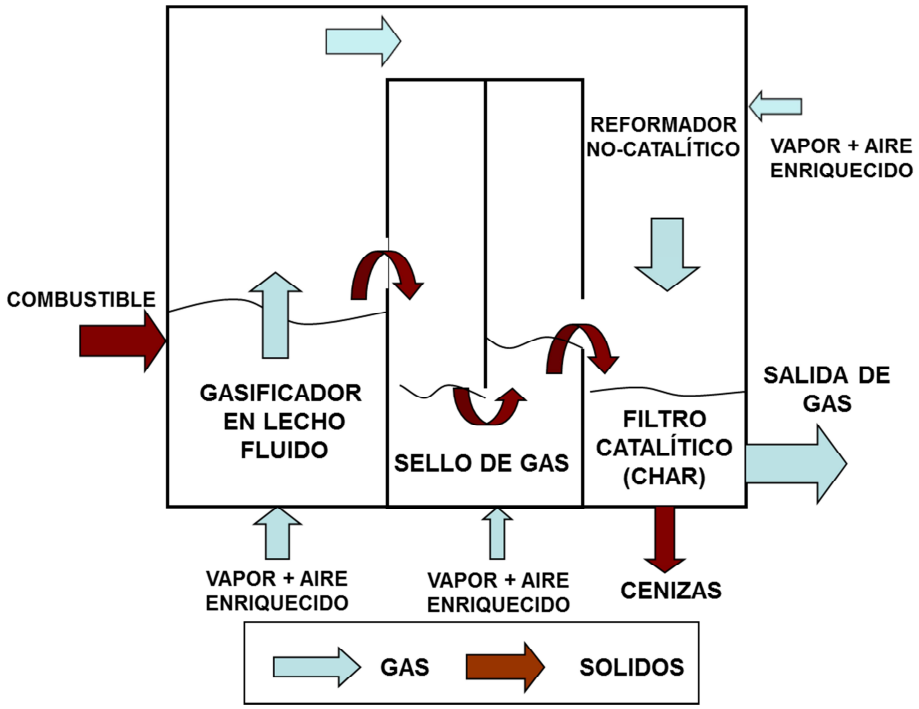


Fig. R-1. Esquema del gasificador en tres etapas

Las tres etapas de las que consta el nuevo diseño son:

Etapa 1- Gasificador en lecho fluido. El objetivo de esta primera etapa es devolatilizar el combustible a una temperatura relativamente baja (del orden de 700-800°C) lo que producirá una mezcla de alquitranes más reactiva que si el proceso se llevara a cabo a mayor temperatura. A la temperatura de esta primera etapa la conversión del carbonizado será poco significativa aún en presencia de vapor.

Etapa 2- Oxidación/reformado no catalítico del gas. En esta segunda etapa el gas producto del gasificador es calentado (hasta una temperatura máxima de 1200°C aprox.) mediante la inyección de una mezcla de aire (o aire enriquecido) y vapor. En esta segunda etapa el objetivo que se persigue es, en primer lugar oxidar/reformar los alquitranes reactivos provenientes del gasificador y, en segundo lugar, incrementar la temperatura del sistema para la tercera etapa.

Etapa 3- Conversión en lecho móvil de carbonizado. En esta etapa se ponen en contacto el gas proveniente de la segunda etapa y el material carbonoso procedente de la primera. Principalmente se producen dos reacciones. En primer lugar la conversión catalítica de los alquitranes que permanezcan en la corriente gaseosa sobre la superficie del material carbonoso y, en segundo lugar, la gasificación del carbonizado restante. Esta etapa es, adicionalmente, un filtro para las partículas que acompañan al gas.

Entre las etapas 1 y 3 existe un sello de gas que permite hacer fluir los flujos de gas y sólido de forma conveniente (ver Fig. R-1). Gracias a este sistema el gas es conducido al reformador no-catalítico mientras que el sólido es transferido directamente de la primera etapa a la tercera. Dicho dispositivo es un lecho fluidizado alimentado en general con vapor y aire, y aunque no es una etapa en sí misma puede permitir cierta flexibilidad en las condiciones (de temperatura y estado de conversión) de entrada del material carbonizado a la tercera etapa mediante el ajuste de la cantidad de oxidante alimentada.

2. Objetivo de la tesis

El objetivo principal en esta tesis es investigar las condiciones de operación del nuevo sistema de gasificación en tres etapas que permitirían reducir la presencia de alquitranes pesados en el gas producto, con el propósito de que éste pueda ser utilizado en un motor para producción eléctrica sin necesidad de tratamientos secundarios intensivos.

La presente tesis aborda el estudio de la formación y la conversión secundaria de alquitranes e hidrocarburos ligeros durante la devolatilización de lodo seco de depuradora en lecho fluido y la influencia de las condiciones operacionales sobre la formación y conversión de estos productos. Esta información será decisiva para el diseño y la determinación de las condiciones de operación de la primera etapa del nuevo sistema. Adicionalmente se estudia la influencia de la temperatura y la concentración de vapor sobre la conversión de ciertos alquitranes aromáticos modelo

(tolueno y naftaleno) sobre diferentes materiales carbonosos (char de carbón, de coco y de lodo seco de depuradora). La información extraída de dicho estudio es empleada para establecer las condiciones operacionales de la tercera etapa del gasificador FLETGAS a partir de la cinética obtenida mediante la simulación del proceso. De los resultados obtenidos se pretenden inferir, igualmente, los principales mecanismos implicados en las transformaciones químicas, en fase gas y sobre material carbonoso, de estos compuestos.

A continuación se presenta un resumen de los capítulos de la presente tesis.

3. Resumen capitular

Capítulo 1: Introducción

En el primer capítulo se presenta la tecnología de gasificación y se enumeran sus ventajas para el tratamiento de biomasas y residuos. Se presentan las diferentes tecnologías de gasificación y se discuten las ventajas e inconvenientes de cada tipo de gasificador llegando a la conclusión de que para sistemas de pequeña y mediana escala enfocados a la producción eléctrica distribuida los equipos que ofrecen más ventajas son los que operan en lecho fluido. En base a las principales limitaciones de este tipo de gasificadores se revisan los diferentes métodos empleados para mejorar el proceso. En base a este análisis se justifica el diseño del nuevo gasificador en tres etapas detallándose la función de cada una de las etapas. Por último se resume el trabajo de investigación contenido en la presente tesis.

Capítulo 2: Experimental

En este capítulo se describen los arreglos experimentales empleados (reactores, sistemas de alimentación de gases, equipos de muestreo, etc…) durante el desarrollo de la presente tesis. De igual modo se detallan los materiales usados (composiciones y propiedades estructurales de combustibles y otros materiales utilizados en los ensayos) y los procedimientos analíticos que se emplean para el análisis de las diferentes muestras generadas. Para el caso particular del análisis de alquitranes se ha incluido un apéndice donde se explican pormenorizadamente los diferentes análisis realizados.

Capítulo 3: Influencia de la temperatura y el vapor sobre los productos generados durante la devolatilización de lodo seco de depuradora en lecho fluido

En este capítulo se estudia la influencia de la temperatura y la presencia de vapor sobre la formación de alquitranes e hidrocarburos ligeros durante la devolatilización en lecho fluido de lodo seco de depuradora. Las condiciones de operación estudiadas incluyen la variación de la temperatura del sistema (uniforme en todo el reactor) entre 600 y 900°C. Este rango engloba aquellas temperaturas habituales en sistemas convencionales de gasificación en lecho fluido (800-900°C) y temperaturas menores a las que se espera trabajar en la primera etapa del nuevo gasificador. El estudio de la

influencia del vapor se realizó en comparando el comportamiento en condiciones de ausencia (atmósfera de nitrógeno) y con una concentración del 30% en volumen.

Las Fig. R-2 y R-3 presentan los resultados más destacables concernientes a la producción de alquitranes bajo las condiciones estudiadas. Los alquitranes aromáticos se encuentran clasificados de acuerdo a su estructura, siendo los de clase 3 compuestos monoaromáticos, los de clase 4 compuestos de 2 y 3 anillos aromáticos y los de clase 5 compuestos de 4 a 7 anillos. Puede observarse como el vapor ejerce una influencia prácticamente despreciable sobre los alquitranes aromáticos (ver Fig. R-2) y tan solo provoca una leve reducción en la producción del alquitrán gravimétrico (medida de la cantidad total de alquitrán condensable a temperatura ambiente que no incluye compuestos ligeros como el benceno, ver Fig. R-3). Sin embargo el incremento de la temperatura provoca una fuerte reducción en la producción de alquitrán gravimétrico a la vez que incrementa la aromaticidad de la mezcla así como el peso molecular de los alquitranes aromáticos.

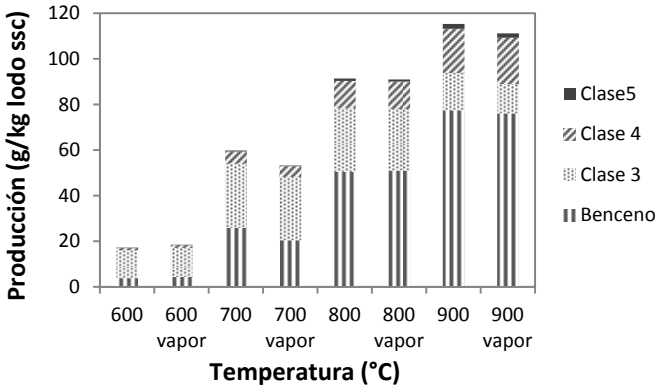


Fig. R-2. Producción de alquitranes aromáticos a diferentes temperaturas del reactor y en presencia y ausencia de vapor.

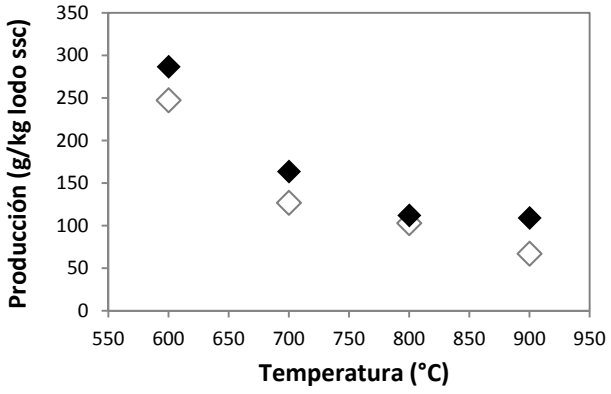


Fig. R-3. Producción de alquitrane gravimétrico en presencia (◇) y en ausencia de vapor (◆)

Comparando las cantidades medidas de alquitrán gravimétrico con la suma de alquitranes aromáticos medidos por cromatografía de gases – espectrometría de masas (GC-MS) se demuestra que una parte importante del gravimétrico, incluso a 900°C, está formado por compuestos no cuantificables por (GC-MS). Este hecho pone de manifiesto que las estimaciones de puntos de rocío realizadas en base a análisis cromatográficos pueden incurrir en importantes errores dado que estos compuestos no-cuantificables pueden ejercer una importante influencia en el valor del punto de rocío. El análisis elemental del alquitrán gravimétrico pone de manifiesto la importante proporción de compuestos heteroatómicos en esta mezcla, siendo destacable la elevada proporción de nitrógeno a altas temperaturas (800-900°C).

Adicionalmente se han obtenido interrelaciones entre las producciones de ciertos hidrocarburos ligeros (cuya medida es simple y puede realizarse on-line) y ciertas familias de alquitranes (cuyo muestreo y análisis es lento y costoso). Por lo tanto estas relaciones pueden suponer un importante ahorro de esfuerzo y dinero para la estimación de las propiedades y concentración de los alquitranes generados. Como muestra se presenta en la Fig. R-4 la relación entre la producción de acetileno y la de alquitranes de la clase 5 (aromáticos pesados). Puede observarse la relación lineal entre las producciones de ambos compuestos en todo el rango de temperaturas analizado.

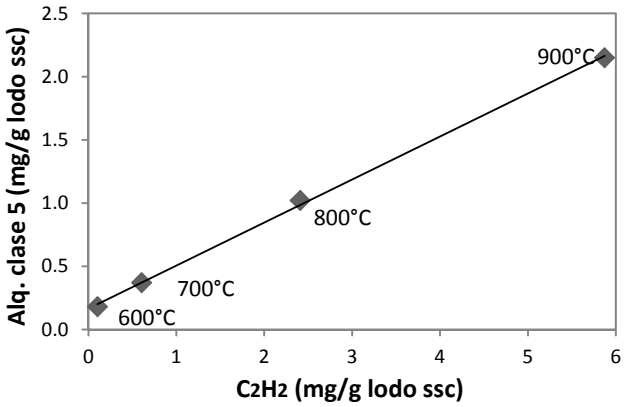


Fig. R-4. Producción de alquitranes clase 5 en función de la producción de acetileno. La línea sólida representa la recta de ajuste.

Capítulo 4: Formación y conversión secundaria de volátiles en lecho fluido

En el capítulo 4 se amplía el estudio sobre la formación y conversión de volátiles iniciado en el capítulo 3 a sistemas de gasificación con diferente temperatura en el lecho fluido y en la zona del reactor con menor (o nula) presencia de partículas (freeboard). Este estudio es de interés debido a que en un sistema con adición estratificada de agente fluidizante es posible conseguir diferencias de temperaturas entre dichas zonas que afecten a la composición del alquitrán producido. Por un lado se investiga la influencia de la temperatura del lecho fluido minimizando al máximo la conversión secundaria de alquitranes e hidrocarburos, es decir, se trata de identificar

la composición de los volátiles (compuestos primarios) que son emitidos por la partícula de combustible minimizando su conversión térmica secundaria. Para minimizar dicha conversión secundaria la temperatura del freeboard se mantiene baja (600°C) mientras que la temperatura del lecho denso se varía entre 500 y 800°C. Por otro lado se estudia la influencia de la temperatura del freeboard durante la conversión secundaria de los alquitranes generados en lecho fluido (lecho denso) a 500°C. Para estas experiencias la temperatura del freeboard se varía entre 600 y 800°C.

La influencia del tamaño de partícula del DSS (entre 1 y 5 mm) también se estudia en el presente capítulo encontrándose que su influencia sobre los diferentes productos de la devolatilización es despreciable. Por último se compara, para ciertas condiciones experimentales, la composición de los volátiles generados por partículas de DSS y de madera (un combustible ampliamente estudiado). De esta comparación lo más destacable es la mayor producción de alquitranes gravimétricos por parte del DSS y la escasa diferencia en la producción de alquitranes de las clases 4 y 5. Este último hallazgo permite suponer que la producción de alquitranes poliaromáticos depende principalmente de las condiciones térmicas del reactor y en menor medida del tipo de combustible utilizado.

Las Fig. R-5 y R-6 presentan el efecto de la temperatura del lecho fluido (lecho denso) sobre los alquitranes aromáticos y gravimétricos. Puede observarse cómo dicha temperatura afecta relativamente poco a la composición y cantidad de alquitrán a temperaturas inferiores a 700°C, siendo dicha influencia algo superior a 800°C. Es destacable que la proporción de alquitranes aromáticos pesados (clase 5) no varía prácticamente con la temperatura del lecho. Este resultado sugiere que bajos tiempos de residencia del gas a la temperatura del lecho limitan el crecimiento de alquitranes aromáticos que dan como resultado PAH pesados. Por lo tanto la combinación de altas temperaturas y bajos tiempos de residencia puede ser una alternativa a tener en cuenta para mantener baja las producciones de alquitrán gravimétrico y de compuestos aromáticos pesados.

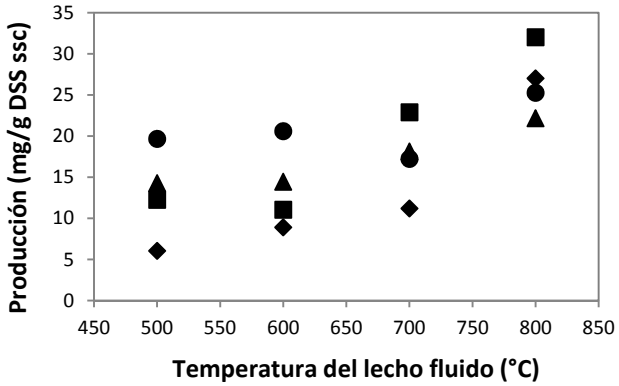


Fig. R-5. Producción de alquitranes aromáticos en función de la temperatura del lecho fluido manteniendo el freeboard a 600°C. Producción de benceno x2 (◆), alquitrán de clase 3 (▲), alq. clase 4 x10 (■) y alq. clase 5 x100 (●).

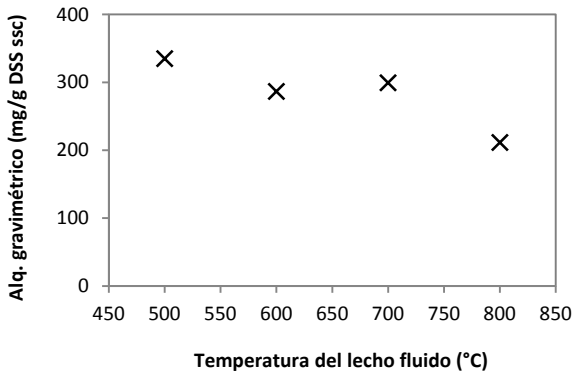


Fig. R-6. Producción de alquitrán gravimétrico en función de la temperatura del lecho fluido manteniendo el freeboard a 600°C.

Las Fig. R-7 y R-8 presentan la influencia de la temperatura de conversión secundaria (temperatura del freeboard) sobre los alquitranes generados en lecho fluido a 500°C. Bajo estas circunstancias el incremento de la temperatura ejerce una importante influencia sobre la composición del alquitrán aumentando la proporción de alquitranes aromáticos de alto peso molecular (PAH) y disminuyendo la producción de alquitrán gravimétrico. Por lo tanto la composición final del gas tras un tratamiento térmico contendrá una baja concentración de alquitranes pero de elevado peso molecular y aromaticidad.

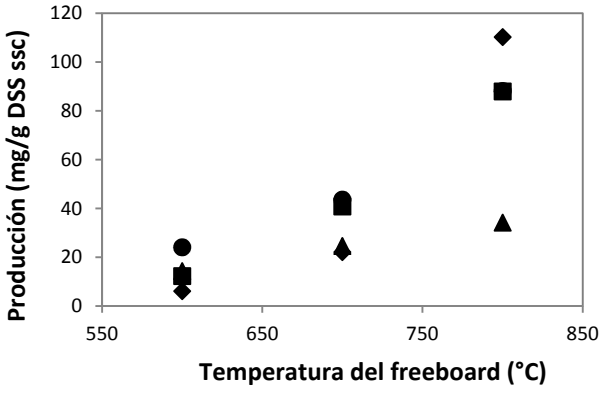


Fig. R-7. Producción de alquitranes aromáticos en función de la temperatura del freeboard manteniendo el lecho fluido a 500°C. Producción de benceno x2 (◆), alquitrán de clase 3 (▲), alq. clase 4 x10 (■) y alq. clase 5 x100 (●).

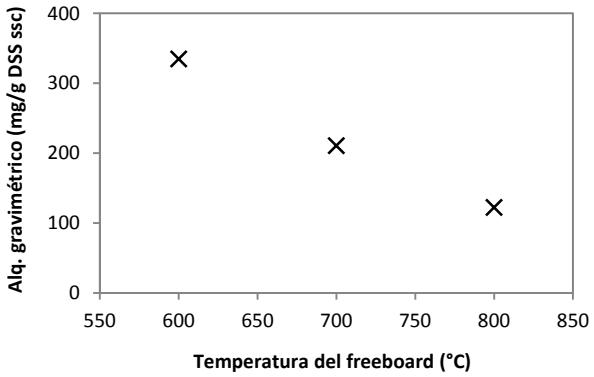


Fig. R-8. Producción de alquitrán gravimétrico en función de la temperatura del freeboard manteniendo el lecho fluido a 500°C.

En un último apartado se analiza la validez de las relaciones entre alquitrán e hidrocarburos ligeros encontradas en el Capítulo 3 en condiciones diferentes a las que fueron obtenidas. Como resultado de este análisis se concluye que las condiciones de operación afectan a las relaciones alquitrán-hidrocarburos y, aunque las desviaciones son en bastantes casos asumibles para obtener de forma aproximada la composición del alquitrán, en otros casos las desviaciones pueden ser significativas.

Capítulo 5: Conversión de alquitrán sobre material carbonoso

En este capítulo se estudia la conversión de dos alquitranes modelo, tolueno y naftaleno, sobre diferentes materiales carbonosos (char de carbón, char de coco y char de DSS). Los alquitranes modelo elegidos son, respectivamente, los de menor peso molecular de los grupos alquil-aromáticos y los PAH. La elección de estos dos compuestos se debe a que se ha demostrado que la actividad del char para convertir alquitranes depende del peso molecular de este último siendo mayor la actividad a mayor peso molecular. Por lo tanto es de esperar que las conversiones alcanzadas por los dos alquitranes seleccionados marquen un nivel mínimo de conversión para cada familia. Los materiales carbonosos elegidos son representativos de diferentes estructuras internas con objeto de determinar el efecto de ésta sobre la conversión de alquitranes. Un material no carbonoso ni poroso (CSi) fue elegido como material de referencia. Los ensayos fueron realizados a temperaturas entre 750 y 950°C y concentraciones de vapor entre 0 y 25%.

Las condiciones experimentales ensayadas han tratado de reproducir el rango de dichas condiciones en las que se ha previsto que opere el filtro catalítico de char presente en la tercera etapa de sistema FLETGAS. Dado que el char en dicho dispositivo estará expuesto durante un periodo de tiempo relativamente largo a la corriente de gas producto, el estudio realizado pretende determinar la variación de la actividad del char con dicho tiempo, esto es, la posible desactivación del material. El valor final del tiempo de residencia del sólido en la tercera etapa del FLETGAS dependerá del tiempo de residencia del gas necesario para alcanzar una conversión

suficiente de alquitranes pesados. La simulación del proceso permitirá estimar dicho tiempo y la conversión de carbono que se alcance en dichas condiciones.

El trabajo realizado ha permitido poner de manifiesto la escasa influencia de la estructura interna del char tanto sobre la conversión de alquitrán como sobre el proceso de desactivación del mismo, ya que para los tres materiales se han obtenido resultados similares (tanto de velocidades de conversión de alquitrán como del proceso de desactivación) pese a las diferencias en su estructura interna. Por el contrario el incremento de la temperatura del proceso y, en menor medida, de la concentración de vapor, aumenta la conversión del alquitrán, reduciendo por tanto la desactivación. Este hecho se explica en base al mecanismo descrito en la Fig. R-9. A bajas temperaturas (o nula presencia de vapor) la velocidad de deposición del alquitrán es superior a la velocidad de gasificación del coque formado sobre el material. Esta deposición de carbono termina por cubrir los centros activos del material donde preferentemente se convierte el alquitrán. A mayores temperaturas (y concentraciones de vapor) la velocidad de gasificación es superior a la de deposición y el material mantiene su actividad.

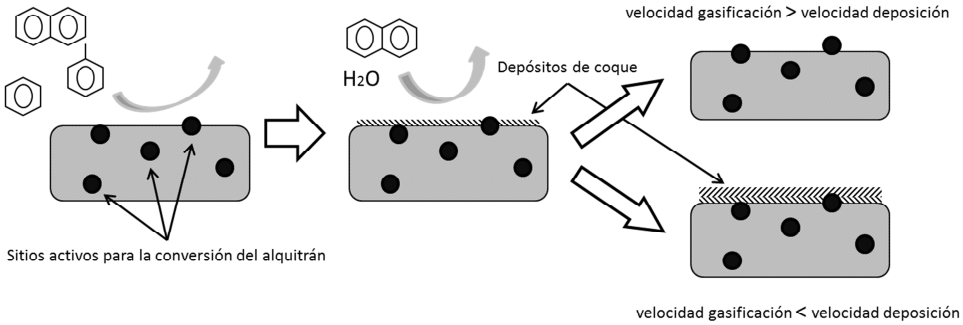


Fig. R-9. Representación del mecanismo de conversión de alquitrán sobre material carbonoso.

Los resultados experimentales obtenidos para diferentes materiales carbonosos son ajustados a una ecuación cinética de carácter empírico, que considera la desactivación del material. La Fig. R-10 compara para uno de los materiales y uno de los alquitranes modelos (tolueno) los resultados experimentales (marcadores) y los del modelo cinético (líneas continuas).

En (Nilsson et al., 2012a) el sistema FLETGAS fue simulado usando una cinética de conversión de tar sobre char tomada de la literatura. Dicha cinética, aparte de haber sido obtenida para un material (char) diferente al que se espera obtener en el sistema, no consideraba la desactivación del mismo. En el presente trabajo se ha implementado la cinética obtenida en la simulación del proceso FLETGAS. La Fig. R-11 compara la conversión de naftaleno alcanzada para ambas simulaciones. Como puede comprobarse la implementación de la cinética aquí obtenidas reduce moderadamente la conversión de naftaleno alcanzada en el lecho para una longitud determinada.

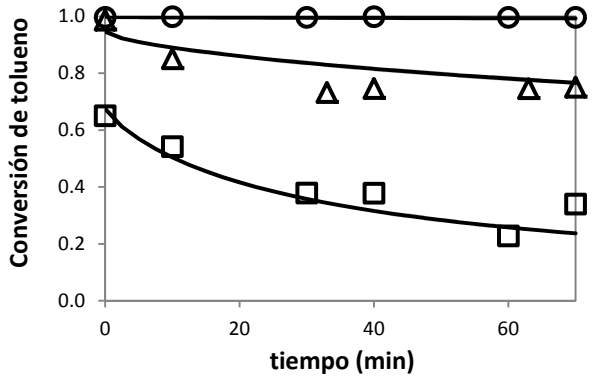


Fig. R-10. Comparación entre la conversión de tolueno sobre char de carbón experimental (marcadores) y del modelo (línea continua) a varias temperaturas y concentración de vapor del 15 vol%; □: 750°C, △: 850°C, ○: 950°C.

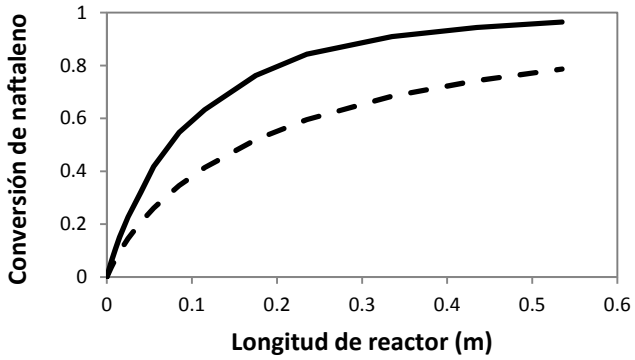


Fig. R-11. Comparación entre la conversión de naftaleno alcanzada en la tercera etapa del FLETGAS en la simulación realizada con datos de la literatura (línea continua) y la simulación realizada con las cinéticas obtenidas en esta tesis (línea de guiones).

Capítulo 6: Conclusiones

En el último capítulo se resumen los hallazgos y conclusiones más relevantes del trabajo realizado y en base a éstas se sintetizan las principales recomendaciones para el diseño y operación del sistema FLETGAS encaminadas a la obtención de un gas apto para su combustión en un motor. Por otro lado se proponen trabajos complementarios a los contenidos en la presente tesis que serán desarrollados en los próximos meses.

4. Conclusiones

El trabajo realizado durante la presente tesis se ha dividido en dos bloques principales con objeto de estudiar la producción y conversión de alquitranes e hidrocarburos

durante la devolatilización de combustible en lecho fluido (Capítulos 3 y 4) y durante el tratamiento del gas sobre un lecho fijo de char (Capítulo 5). Estos estudios responden a la necesidad de determinar las condiciones de operación del sistema FLETGAS que permitan eliminar la presencia de alquitranes pesados en la corriente de salida. En concreto el estudio de los Capítulos 3 y 4 va encaminado a determinar la influencia de las condiciones de operación (temperaturas, diferenciación térmica en dos zonas del devolatilizador, presencia de vapor, etc…) sobre los productos generados en el lecho fluido (primera etapa). Por su parte el Capítulo 5 está enfocado a apoyar el diseño del filtro catalítico de char (tercera etapa) donde se espera que sean convertidos los alquitranes pesados.

Las principales conclusiones extraídas de este trabajo son:

- La presencia de vapor no afecta apreciablemente a la concentración de alquitranes aromáticos o hidrocarburos generados el lecho fluido a temperaturas entre 600 y 900°C. Sin embargo un incremento en la temperatura del reactor de 600 a 900°C reduce significativamente la producción de alquitrán gravimétrico y aumenta su aromaticidad. La producción de hidrocarburos ligeros saturados aumenta entre 600 y 700°C, disminuyendo a mayores temperaturas, mientras que los insaturados (y el metano) ven incrementada su producción al aumentar la temperatura de 600 a 900°C.

- Se ha encontrado que existen ciertas correlaciones entre las cantidades de alquitrán e hidrocarburos producidas durante la devolatilización del combustible. Las correlaciones encontradas relacionan las producciones de metano y benceno, metano y alquitrán de la clase 4 y etileno y alquitrán de la clase 5. Estas correlaciones pueden ser de utilidad para estimar la composición del alquitrán generado a partir de medida de hidrocarburos ligeros, y por tanto sin necesidad de costosos muestreos y análisis de alquitranes.

- La temperatura a la que se someten los volátiles tras su formación (conversión secundaria) tiene una mayor relevancia sobre la composición final del alquitrán que la temperatura a la que es devolatilizada la partícula (temperatura del lecho denso de partículas).

- El análisis elemental del alquitrán gravimétrico ha puesto de manifiesto que existe una elevada proporción de compuestos heteroatómicos (principalmente oxigenados y nitrogenados) incluso a temperaturas elevadas (800-900°C). Dado que estos compuestos son difícilmente cuantificables con las técnicas habituales de análisis (GC-MS) las estimaciones del punto de rocío realizadas en base a dichos análisis pueden infra-estimar el valor real.

- El tamaño de partícula del lodo seco de depuradora (DSS) entre 1 y 5 mm apenas tiene influencia sobre la composición del alquitrán generado durante la devolatilización en lecho fluido a 800°C.

- El origen del combustible afecta sensiblemente a la producción total de alquitranes. Sin embargo la producción de compuestos aromáticos pesados depende principalmente de las condiciones térmicas del reactor habiéndose encontrado producciones similares de estos compuestos utilizando diferentes combustibles (DSS y madera) si las condiciones del sistema se mantienen constantes.

- La estructura interna inicial del carbonizado tiene una influencia escasa sobre su actividad en la conversión de alquitranes, es decir, carbonizados con diferente estructura interna alcanzan conversiones similares de alquitrán. El proceso de desactivación es igualmente independiente de dicha estructura interna inicial.

- Temperaturas de 850°C o superiores y tiempos de residencia de 0,3 s son suficientes para alcanzar conversiones completas de ambos alquitranes (tolueno y naftaleno) si el char no está desactivado.

- La desactivación del carbonizado durante la conversión de alquitrán es prácticamente despreciable siempre que se mantengan condiciones que favorezcan una velocidad de consumo de carbono superior a la velocidad de deposición. Temperaturas superiores a 950°C y concentraciones de vapor del 15 vol% evitan la desactivación del char. Este hecho permite inferir que la actividad del carbonizado reside en centros activos (probablemente metales alcalino y alcalino-térreos) presentes en la estructura del carbonizado de origen.

- La simulación del sistema FLETGAS utilizando la cinética de conversión de naftaleno sobre carbonizado de DSS demuestra que el sistema reduce eficazmente la concentración de dicho compuesto en el gas de gasificación. Dado que el compuesto estudiado, naftaleno, es el menos reactivo de los alquitranes pesados, es de esperar que el gas producido por el nuevo gasificador en tres etapas cumpla los requerimientos de limpieza para poder ser usado en motores de gas para producción eléctrica.

- El gasificador FLETGAS deberá operar sin adición de vapor en la primera etapa debido a su escasa influencia sobre la conversión de alquitranes. El gas producto de esta primera etapa deberá ser oxidado/reformado en la segunda etapa con el doble objetivo de reducir la concentración de alquitrán y de elevar su temperatura para prevenir la desactivación del char en el lecho móvil de la tercera etapa.

Studies on tar formation and conversion for the development of a three stage gasifier

CHAPTER 1

Introduction

1. Introduction

The rising energy demand and the increasing environmental upsets associated with the climate change have promoted the searching for new energy sources with lower environmental impact. The use of biomass and waste for power production is an alternative to the use of fossil fuels due to their lower impact on the global CO_2 emissions.

The use of woody biomass for power or chemicals production is an interesting alternative to fossil fuels due to its high global production and the low content in sulfur and ashes. However wood is a relatively expensive energy source making more interesting the use of alternative and cheaper non-woody biomass materials and wastes. However these fuels have disadvantages, such as the higher content of ash and of other inorganic contaminants like sulfur, chlorine, AAEM or heavy metals (van Paasen et al., 2006; Mun et al., 2009).

Gasification technology is a thermochemical process for the conversion of solid fuels into gas at high temperature using sub-stoichiometric oxygen (partial oxidation). This technology permits the transfer of the energy contained in the solid fuel to the product gas, which can be used in a variety of applications (Gómez-Barea & Leckner, 2009). Gasification of biomass and waste is similar to that of coal in the sense that biomass can be regarded as a young coal (Highman & van der Burgt, 2008). Essentially, biomasses and wastes contain more oxygen and volatiles (and often more moisture) than coal, and the nature of the ashes differs substantially from coal ash.

There are three main types of gasifier: fixed or moving bed, fluidized bed, and entrained flow. Fixed-bed designs are basically updraft (countercurrent) or down-draft (cocurrent). In updraft gasifiers the solid carbon in the fuel is almost completely converted but gas leaves the reactor near the pyrolysis zone where the content of heavy organic components (tar) in the gas is higher. Updraft gasifiers can be used for wet fuels and are relatively insensitive to the fuel size. In downdraft (concurrent) gasifiers, the fuel and gasification agent flow in the same direction and the gas leaves the reactor near the hottest zone, which makes the tar concentration much lower than in updraft gasifiers. However the fuel fed to downdraft bed gasifiers must meet certain requirements (particle size distribution, moisture, etc.) (Kurkela et al., 2004). In both updraft and downdraft gasifiers the maximum size is limited to a few MW because of the problem of maintaining a regular conversion front in a wide fixed bed (Gómez-Barea & Leckner, 2010).

In entrained-flow gasifiers the high temperature employed allows production of a gas that is almost free from tar with nearly complete carbon conversion. However, there are a few drawbacks associated with the processing of biomass in this application: the difficulties of economical particle size reduction of some biomasses and wastes and the corrosion of the reactor lining caused by the aggressive nature of molten slag from biomass.

Gasification in fluidized bed (both bubbling and circulating) has several advantages over that in a fixed/moving bed or an entrained-flow gasifier for small to medium size gasifiers (Gómez-Barea & Leckner, 2010). The fluidized bed provides high mixing and reaction rates, accommodates variation in fuel quality and allows scaling-up of the process. Various concepts based on fluidized beds have been developed for gasification. Stand-alone, air–blown, bubbling fluidized-bed gasification is the simplest, directly–heated design, but it delivers a gas diluted by nitrogen, having low heating value (4-6 MJ/Nm^3) and high tar content (10-40 g/Nm^3). In addition up to 10% of the energy in the fuel is lost by the carbon discharged with the ash caused by the relatively low char conversion achieved in the gasifier (typically below 70%, Gómez-Barea et al., 2012). Medium heating-value gas (12-15 MJ/Nm^3) can be produced using steam as gasification agent. For this purpose two approaches have been developed: directly heated gasifier, in which a mixture of oxygen and steam is introduced in one single reactor (Rauch et al., 2004), and indirectly heated gasifier, consisting of two reactors using air in one (char combustor) and steam in the other (Paisley & Overend, 2002).

In all types of FBG the tar concentration in the gas is high, since the process temperature is kept relatively low to prevent agglomeration and sintering of bed material (Gómez-Barea & Leckner, 2009; Highman & van der Burgt, 2008; Gómez-Barea & Leckner, 2010). The unconverted char reduces the efficiency of the process and the high concentration of heavy tars limits the application of the gas to direct thermal applications, like burning in kilns and boilers. For power production in gas engines the product gas must be cooled down to 30-40°C. In this case the main requirement is to achieve a tar dew point below this temperature in order to avoid the blocking of the lines produced by tar deposition. The acceptable limit for tar is usually expressed on the basis of total tar concentration. However, it has been demonstrated that for engine application the tar dew point is a more appropriate parameter. Gas

containing 100 mg/Nm^3 of tar with a dew point above 70°C has been found to cause engine problems (Gómez-Barea & Leckner, 2009). Conversely, gas with a tar concentration above 5 g/Nm^3 has been used in engines without technical problems (Gómez-Barea et al., 2012). This shows that the nature of the tar, and not the tar concentration, is the key parameter for assessment of the suitability of a gas for engine application.

In summary, direct oxygen-blown entrained-flow gasifiers produce a gas with minimum tar content and the char can be fully converted. However, economy makes such concepts non-viable for small and medium scale gasifiers. Indirectly-heated FBG convert most of the char, but the tar content of the gas is similar and the cost is increased with respect to air-blown FBG. It can be concluded that the development of gasification of biomass and waste for the production of distributed electricity requires improvement of current stand-alone, air-blown, FBG. Assessment of technical and economical methods to improve the performance of such systems has been made in (Gómez-Barea et al., 2012).

Fig. 1.1 illustrates the problem of optimizing an FBG: raising the temperature increases tar and char conversion, but the danger for sintering of ash and bed material also increases and sets a maximum temperature, which mainly depends on the fuel. Considering the balance between benefits and drawbacks associated with the thermal level, the temperature range for the operation of a biomass gasifier is between 800 to 900°C. However even at the highest temperature acceptable, it is difficult to convert heavy tar compounds in the reactor.

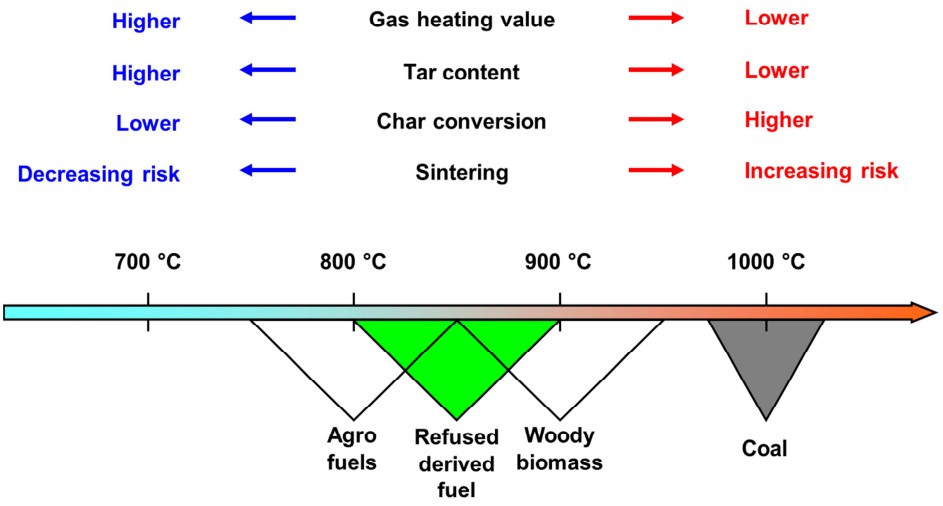


Fig. 1.1: Effect of temperature on parameters and processes during gasification. Adapted from (Devi et al., 2003).

Different strategies have been addressed aiming at reducing the tar concentration in the gas product. These strategies can be classified into primary and secondary measures (van Paasen, 2004). Secondary methods are those removing (or converting)

the tar downstream the gasifier. These methods include physical removal of tars (water or oil scrubbers, filters and electrostatic precipitators), downstream catalytic reactors (Ni-based or mineral catalysts among others) and thermal reactors (Han & Kim, 2008). This way to clean the gas is, however, too complex and expensive for small or medium-size plants (Gómez-Barea & Leckner, 2009).

Primary measures are those converting the tar within the gasifier and include the selection of operation conditions, the use of additives in-bed and the adequate gasifier design. The use of in-bed catalysts have demonstrated to achieve moderate reductions in the tar concentration (Safitri, 2005; Sutton et al., 2001) but the tar dew point seems to be hardly affected (Campoy et al., 2010). It is concluded that efforts should be focused on the design of novel gasification methods to achieve higher char and tar conversion, increasing the process efficiency and reducing the complexity of secondary gas cleaning.

2. Fundamentals of fuel conversion in FBG

A biomass particle fed to a gasification reactor undergoes a series of conversion processes, listed in Table 1.1. The fluidization gas is, in general, a mixture of steam, oxygen, nitrogen and carbon dioxide (nitrogen is present in air-blown FBGs, whereas carbon dioxide could be part of the input gas in a gasifier integrated in an oxy-fired plant, intended for carbon-capture). Initially, the fuel particle is dried and devolatilized (R1) yielding char and volatiles. Subsequently, volatiles (R7-9) and char (R2-3) may be oxidized, and finally, char may be gasified by carbon dioxide, steam and hydrogen (R4-6). Fuel particles shrink, and primary fragmentation may occur immediately after the injection of the fuel into the bed. Secondary fragmentation and attrition of char take place together with char conversion. The energy for heating the fuel to reactor temperature and for satisfying the needs of the endothermic reactions is provided by the partial combustion of the fuel in autothermal gasification. The volatiles include non-condensable gases, such as CO_2 or H_2, condensable gases (tar), and water (chemically bound and free water). After primary decomposition, a variety of gas-gas and gas-solid reactions (secondary conversion) take place during which the tar may oxidize (R11), reform (R12 and R13), and further react by cracking (R15). Thermal cracking of tars may include different reactions like dealkylation, decarboxylation, aromatization and formation of soot by polymerization. Primary and secondary tar conversion processes can be homogeneous and heterogeneous, occurring inside as well as outside of the fuel particle. The tar conversion can be catalyzed by solids added to the bed (dolomite, olivine, etc) or simply by the carbonaceous surfaces in the devolatilizing particles.

The conversion of char and tar is related to the effective time of reaction with gas and catalysts, which in turn depends on the residence time of fuel and char particles in the bed and on the local mixing conditions (Petersen & Werther, 2005b). Of particular importance is the contact between char and tar with oxygen and steam and the position where the fuel particle is devolatilized. Formation of bubbles, bypassing of gas, entrainment of material and other factors influence the reaction time (Gómez-

Barea & Leckner, 2010; Petersen & Werther, 2005b). The key operation parameter in an FB is the superficial gas velocity and the properties of the fuel particle (mainly size and density), determining the degree of mixing and entrainment in the reactor (Gómez-Barea & Leckner, 2010; Souza-Santos, 2004). High superficial velocity improves solids mixing, but biomass particles with lower density and larger size than the bed particles can still be non-uniformly distributed.

During devolatilization the fuel is decomposed into three main fractions: light gas (non-condensable), solid carbonaceous material containing ash and fixed carbon (char) and a heterogeneous mixture of organic components (tars) (Gómez-Barea & Leckner, 2009). General trends of devolatilization can be determined by comparison of published data, as it is shown in Fig. 1.2, where the yields of char, light gas, and liquids (tar + water) as a function of temperature at various heating rates are presented for a great deal of biomass materials (Neves et al., 2011). Despite the scatter in the data, due to the variety of biomass fuels and research rigs included in the analysis, the main trends can be observed.

Table 1.1: Main reactions in the biomass gasification process

Stoichiometry	Standard Heat of reaction (kJ/mol)	Name	Nr.
Biomass devolatilization			
Biomass → char + tar + H_2O + light gas (CO + CO_2 + H_2 + CH_4 + C_{2+} + N_2 +…)	endothermic	Biomass devolatilization	R1
Char combustion			
C + ½ O_2 → CO	-111	Partial combustion	R2
C + O_2 → CO_2	-394	Complete combustion	R3
Char gasification			
C + CO_2 → 2CO	+173	Boudouard reaction	R4
C + H_2O → CO + H_2	+131	Steam gasification	R5
C + 2H_2 → CH_4	-75	Hydrogen gasification	R6
Homogeneous volatile oxidation			
CO + ½ O_2 → CO_2	-283	Carbon monox. oxidation	R7
H_2 + ½ O_2 → H_2O	-242	Hydrogen oxidation	R8
CH_4 + 2O_2 → CO_2 + H_2O	-283	Methane oxidation	R9
CO + H_2O → CO_2 + H_2	-41	Water gas-shift reaction	R10
Tar reactions (tar assumed C_nH_m)			
C_nH_m + (n/2)O_2 → nCO + (m/2)H_2	endothermic (except R11) (200-300)	Partial oxidation	R11
C_nH_m + nCO_2 → (2n)CO + (m/2)H_2		Dry reforming	R12
C_nH_m + nH_2O → nCO + (n+m/2)H_2		Steam reforming	R13
C_nH_m + (2n-m/2)H_2 → nCH_4		Hydrogenation	R14
C_nH_m → (m/4)CH_4 + (n-m/4)C		Thermal cracking	R15

At the lowest temperatures (<300°C) char is the main product. At middle-range temperatures (450-550°C) a maximum is observed for liquids. Qualitatively, these general trends in product yield as a function of temperature are the same for slow and fast heating rates. On heating up to around 450-550°C, slow heating rates give more char and less tar than fast heating rates due to intraparticle charring of the primary tars and the low activity of secondary reactions of volatiles. The observed decrease in the yield of char with temperature indicates that the major mass loss of fuel occurs in the range of 200-600°C, i.e. most gas is released from the solid fuel. At these low temperatures, the heating rate has a small influence. As temperature increases above 450-550°C the variation in the yield of char is small, with low heating rates generally associated with higher yield of char. Temperature and heating rate (particle size) also determine the physical properties of the primary char, which in turn influences the chemical reactivity of the char and its fragmentation properties. The influence of the heating rate on the tar yield becomes less important at the highest temperatures analyzed (>800°C).

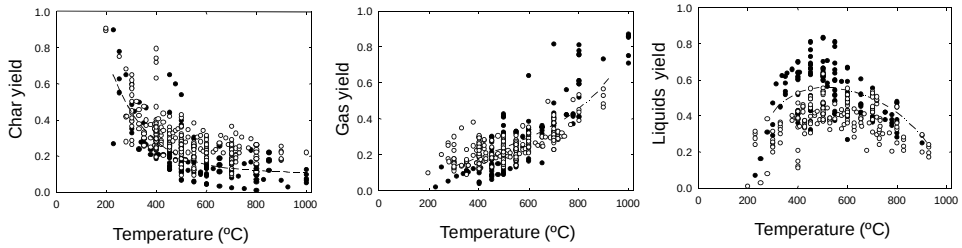


Fig. 1.2: Yields of char, light gas and total pyrolytic liquids (tar +water) as a function of the peak pyrolysis temperature. ● -"fast heating rate"; ○ -"slow heating rate"; ··–·· empirical model (Gómez-Barea et al., 2013; who adapted data taking from Neves et al., 2011).

Thermal decomposition of mm-sized particles in an FBG is referred to as primary pyrolysis, occurring in the lower range of temperature during the heating up of a particle (300-500°C). Thereafter, at bed temperature in a single-stage FBG (800-900°C), when most volatile matter has been released, secondary conversion takes place, characterized by the oxidation and reforming of gas and tar in the gasifier. The conversion of the char takes place mostly by gasification with CO_2 and steam, since O_2 is consumed by the gas.

A simplified description of the fuel conversion can be made by splitting the aforementioned processes into sequential steps: primary generation and secondary conversion of volatiles. Fig. 4.1 in Chapter 4 depicts the main process involved from the particle injection to the final gas produced following this two-steps simplified approach. The distinction made between primary and secondary processes is an approximate method to track the conversion of volatiles allowing the development of FBG models with reasonable complexity, useful for optimization of the operating conditions.

The primary volatiles emitted from a coarse particle react and change their chemical nature both during the way out from the particle and in the emulsion of the FB (outside the particle). The extent of these changes depends on the operating condition in the gasifier, which can be adjusted by variables such as biomass particle size, air/biomass ratio, staging of the fluidization agents along the gasifier and the use of in-bed catalyst. Then, the analysis of how the reactor conditions affect the devolatilization yields can be useful in order to select operating conditions to optimize the yield of tar compounds in the gas mixture and its composition. In Chapter 3 and 4 of this thesis these questions are investigated by experiments in a laboratory fluidized beds, where the composition of the fluidization agent and the thermal level of the gasifier are varied to analyze the changes in tar composition and other parameters.

3. Tar formation and conversion in FBG

Tar is defined as all organic compounds, produced during the thermochemical conversion of solid fuels, with a molecular mass larger than benzene (excluding soot and char) (van Paasen, 2004). This definition includes a complex mixture of organic compounds with a wide range of mass, whose composition and reactivity changes during the conversion process (Evans & Milne, 1987).

Under typical operation of an autothermal FBG, the amount of oxygen blown to the reactor is typically less than 30% of that required for complete combustion of the fuel. Light gases like hydrogen, carbon monoxide or methane are the major products at gasification temperatures of 750-900°C, however heavier organic compounds (tars) are also present in the product gas.

The tar compounds generated during devolatilization suffers several transformations on its way out of the fuel particle and, once evolved, in the reactor environment where higher temperatures or the presence of additives can drastically modify the composition and yield of tars and light hydrocarbons. For mm-sized particles, the devolatilization rate is normally limited by the intra-particle heat transfer, so the devolatilization takes place at temperature below that of the emulsion of the FB where the particle is immersed (400-600°C). At this temperature the fuel is mainly decomposed in fragments of its original structure containing a high proportion of aliphatic chains and heteroatoms (O, N or S). These chemical structures are thermally unstable and decompose rapidly when meeting higher temperatures in their way out of the particle and in the gasifier atmosphere. The decomposition of the primary tars leads to light gases such as CO, CO_2 or light hydrocarbons and aromatic compounds produced by the rearrangement of aliphatic structures. These tars are abundant in gasifiers operating between 700 and 800°C. At higher temperatures the aromatic structures loss the attached functional groups (mostly aliphatic chains and hydroxyl groups) by C-C bond scission reactions and the aromatic compounds polymerize to produce PAH. Fig. 1.3 summarizes the influence of the reactor temperature on tar composition by lumping the tars into four classes namely: primary (parent fuel fragments), secondary (alkyl phenols and olefins), alkyl-tertiary (alkyl-aromatics) and condensed tertiary (PAH) (Milne et al., 1998).

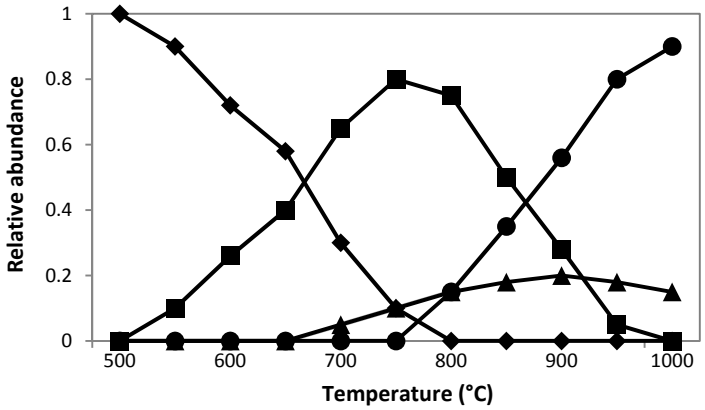


Fig. 1.3. Distribution of the four tar classes as a function of temperature at 0,3s of gas residence time (adapted from (Milne et al., 1998)). ◆: Primary tar, ■: Secondary tar, ▲: Alkyl-tertiary tar, ●: Condensed-tertiary tar.

It is known that the presence of oxygen strongly affects the tar composition (Campoy et al., 2010; Houben, 2004; Pan et al., 1999). However in directly-heated fluidized bed gasifiers the conversion of tar with oxygen is limited because most of oxygen reacts with light gas and, in less extent, with char. In addition, the higher proportion of air is fed at the bottom, promoting the oxygen consumption at the bottom bed, as it has been verified by the high temperature measured in the zone near the distributor in this type of gasifier. Then, the oxygen hardly reaches the bed surface, where the particles devolatilize most of the time. This occurs even in bottom-bed fed FBG, due to the inherent floatability of most biomass during volatile release (Gomez-Barea & Leckner, 2010). As a result, the tar conversion process is mainly driven by the temperature profile inside the gasifier and the composition of the bed solid inventory.

Due to the virtual absence of oxygen in the gasifier, the tar conversion process in FBG can be studied by conducting experiments in the laboratory in pyrolysis conditions, assuming that other compounds like CO_2 or steam do not affect the release of primary products during devolatilization. The latter has been demonstrated by measurements presented in (Nilsson, 2012). The conduction of devolatilization tests with nitrogen and mixtures of nitrogen and steam simplifies the experimental procedure and has been applied in Chapters 3 and 4 of the present work.

4. Review of strategies to convert tar compounds in conventional FBG

A directly-heated FBG of a given type and flow rate of biomass (thermal input) is optimized by adjusting the flowrate of oxygen (air or enriched air), steam and catalyst or additive, if any, to give sufficient temperature and time for char and tar conversion (time for gas mixing and contact with catalysts and char) under the condition of safe operation (without sintering, Gómez-Barea et al., 2013). An ideal gasification process should eliminate the need for further complex gas treatment, and the char should be

completely converted in the gasification reactor. Operational primary measures (without considering the gasifier design) that can be applied in practice are the adjustment of the flow rate and composition of the gasification agent, staging of the gasification agent, and addition of an in-bed catalyst. These measures determine the temperature and gas composition in the different zones of the gasifier, establishing the extent of conversion of volatiles and char along the gasifier. The various measures applied are reviewed below.

Temperature: The rise of temperature is the first measure to be tried, because it is easily achieved by adjusting the oxygen to fuel ratio. The higher this ratio, the higher the temperature, and the more fuel is converted, but also more gas is burnt, lowering the heating value of the product gas. The danger for ash sintering limits the operational temperature to a level where full conversion may not be attained, and the temperature rise should also be weighed against the decrease of the heating value of the gas. On the other hand, the rise in temperature, despite reducing the total yield of tar, increases the concentrations of PAH compounds. The tar composition, rather than the total tar concentration, is the key factor in electricity production where downstream equipment may be affected. Heavy tars (especially heavy PAH tars) are responsible for soot formation and fouling in pipes and in a gas engine. It is demonstrated that up to 900°C, PAHs are not significantly converted inside the gasifier. Similar conclusions have been obtained in other work (Campoy et al., 2008, 2009 and 2010), and the evidence is that no FBG operates without tar problems unless an extensive secondary treatment is applied (Gómez-Barea et al., 2009). We conclude that the temperature at which the fuel is fully converted into gas is not the optimum for electricity production, because the gas has a high dew point and cannot be used in an engine without an extensive secondary treatment.

Steam addition: Char and tar reduction in an air-blown FBG can be improved by adding steam or enriched-air (enriched up to roughly 40% O_2 in volume) steam mixtures. Addition of steam to a directly heated gasifier enhances tar reforming and char gasification, improves the quality of the gas, and reduces its tar content (Campoy et al., 2008 and 2009). However, steam addition reduces the temperature of the gasifier and more oxygen has to be added to maintain the temperature level, lowering the heating value of the fuel gas produced (Campoy et al., 2009). There is an optimal steam to oxygen ratio where steam addition, producing CO and H_2, positively compensates for the burnt fuel gas, because char is further converted (Campoy et al., 2008 and 2009). Steam addition at high temperature is an effective measure (Ponzio et al., 2006), but the temperature of the input steam is limited to that achievable by heat integration (for instance, by heat exchange with the produced gas) if the gasification process is conducted autothermically (no external heat is added).

Air staging: Staging of the gasification agent creates various thermal levels in the gasifier. Staging by injection of secondary air has been tested in conventional FBG at pilot scale (Campoy et al., 2010; Narváez et al., 1996; Pan et al., 1999). In the secondary-air injection arrangement, a portion of the inlet oxygen is conducted to a port in the upper part of the bed or in the freeboard. Fig. 1.4 shows the temperature profile attained in a demonstration FBG (Gómez-Barea et al., 2008). There are two main temperature levels in the gasifier: one in the bed, where the temperature is

highly uniform due to intense mixing, and one in the freeboard, with a temperature that levels off slightly with height. A considerable tar reduction, especially of heterocyclic and light PAH tars (especially naphthalene), from 15 to 5 g/Nm^3, was achieved in that system (Gómez-Barea et al., 2008). However the total tar concentration was still high (a few grams per Nm^3) and the proportion of stable aromatic tar compounds (heavy PAH) in the gas increased significantly. Staging of the gasification agent, oxygen and steam, despite being potentially interesting, has not been reported. In any case, it seems that a more distinct division of zones in the gasifier is necessary to achieve the tar reduction required.

Catalysts: An in-bed catalyst has a great influence on the cracking and/or reforming reactions (Stevens, 2001; Sutton et al., 2001; Simell, 1997; Salo, 2010). Enhancement of local gas and solids mixing is necessary for the efficiency of this primary measure since, if the fuel particles are devolatilized at the bed surface, the interaction tar-catalyst would be negligible. Typical in-bed catalysts are calcined limestone, dolomite, and olivine sand and, less frequently, Ni-based or other metallic catalysts. Reduction of tar by cheap catalysts, such as natural mineral (dolomite, olivine, etc.) reaches concentrations down to 0.5 g/Nm^3. However the tar dew point is less affected and remains still too high for the direct use of the gas in an engine for power production. This result points out that small amounts of heavy tar contribute significantly to the dew point of the gas, and this will cause problems in applications where the gas has to be cooled to the ambient temperature, so this method has to be complemented by secondary treatment. Char can be considered also a catalyst and due to the relevance for the present thesis the use of char as a catalyst for tar conversion is studied separately below.

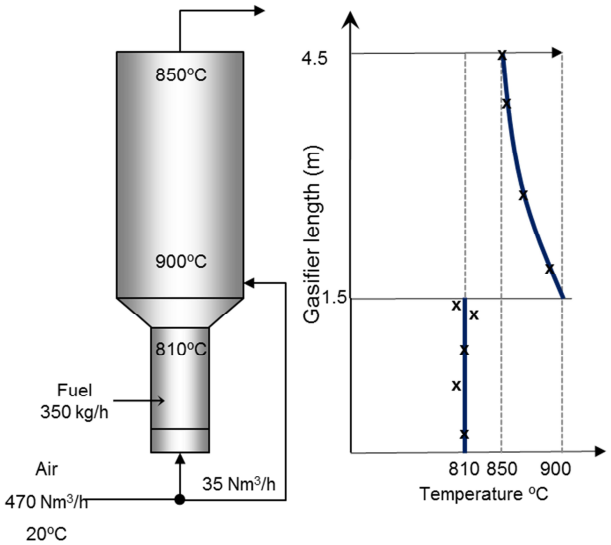


Fig. 1.4. Experimental temperature profile measured in a demonstration FBG with secondary air injection. Data taken from internal reports mentioned in (Gómez-Barea et al., 2008)

Char: The activity of char to convert tars has been demonstrated in several works (Griffiths & Mainhood, 1967; Brandt et al., 2000; Devi et al., 2003; Abu el-Rub et al., 2008; Hayashi et al., 2000; Hayashi et al., 2002; Hosokai et al., 2008; Juneja et al., 2010; Hosokai et al., 2011; Matsuhara et al., 2010). To give a rough idea on the effectiveness of char compared to other catalysts, experimental findings (Abu el-Rub et al., 2008) are illustrated in Fig. 1.5, taking naphthalene as a model compound. The measurements were made in a fixed bed with 0.3 s residence time at 900°C, using two initial naphthalene concentrations (40 and 80 mg/Nm^3). Naphthalene is shown to be thermally stable at 900°C (only 2% was converted over silica sand), whereas it is more converted with dolomite and olivine, and almost fully converted in the presence of nickel-based catalyst and the two chars used. It is concluded that char effectively converts tar compounds in the conditions tested. A secondary, fixed bed reactor, with this material could be effective, but the situation in an FBG differs from that in a fixed bed: the proportion of char is low in standard FBG and the contact of tar with in-situ generated char is difficult due to mass-transfer effects in the gas bubbles and by-passing of gas. It is difficult to achieve a reasonable conversion in a single vessel owing to these fluid-dynamic effects, but staged gasification could make this concept possible.

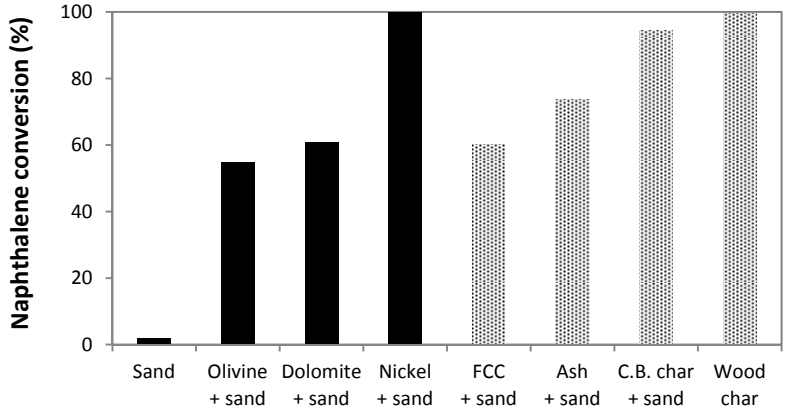


Fig. 1.5. Effect of various catalysts on naphthalene conversion at 900°C, 0.3 s residence time of the gas, feed gas composition: 6 vol% CO_2, 10 vol% H_2O and balance N_2, initial naphthalene concentration: 40 g/Nm^3 (filled bars) and 90 g/Nm^3 (dotted bars). C.B. char: commercial biomass char. Adapted from (Abu el Rub et al., 2008).

The char tested in Fig. 1.5 and other works is not generated in the gasification process but it is acquired from commercially available products or prepared in the laboratory under controlled conditions, these latter being usually different to those in an FB. Moreover, the char is cooled after generation at high temperature in the lab oven and then grinded to the desired particle size.

The alkali and alkaline earth-metals remain in the char structure after generation in a FGB, especially potassium in the form of carbonates, hydroxides or oxides, which affects steam reforming of the nascent tar (Hayashi et al., 2000; Hayashi et al., 2002)

and char gasification process (Matsuhara et al., 2010). Polymerization of PAH compounds promoted at temperatures above 700°C (Hosokai et al., 2008) makes the rate of char gasification with steam lower, whereas the char acts as a tar filter at temperature below 600°C, reducing the tar concentration without being gasified. The deactivation of char by soot formation is then expected at high temperature. In Chapter 5 of the present work this problem is studied.

Summary and conclusion

The impact of the primary measures discussed can be improved if the effect of these measures on different tar compounds is understood (Gómez-Barea & Leckner, 2010; Devi et al., 2003; Kiel et al., 2004; Campoy et al., 2010). As a main conclusion, the combined use of cheap in-bed catalysts (mineral rocks and char), injection of secondary air, and optimization of the composition of the gasification agent in conventional FBG designs, despite improving the process, has been shown to be insufficient to attain the gas quality required in power production with gas engines. It is concluded that further measures involving redesign of the gasifier/process are necessary, i.e. innovative designs should be developed.

5. New developments based on staged gasification

It has been shown that optimization of conventional directly heated FBG is not effective enough to sufficiently reduce the tar dew point to the required level. Indirectly heated gasifiers consisting of twin beds convert most of the char, but the tar problem remains, so it is neither a sufficiently good solution without the use of expensive secondary cleaning of the gas. Therefore, staged gasification in directly−heated gasifiers has been proposed, searching for high conversion of both tar and char in the reactor itself (Wang et al., 2007; Bui et al., 1994; Susanto & Beenackers, 1996; Van der Drift, 2002; Henriksen et al., 2006; den Uil, 2000; Houmoller et al., 1996; Lettner et al., 2007; Schmid & Mühlen, 1999; Hamel et al., 2007).

A few innovative processes have been proposed based on staged gasification in fixed or moving beds (Wang et al., 2007; Henriksen et al., 2006; den Uil , 2000; Houmoller et al., 1996; Lettner et al., 2007; Schmid & Mühlen, 1999; Hamel et al., 2007). In order to carry out staged gasification in FB, enabling high throughput and flexibility, a new staged-gasification concept is under development by the Bioenergy Group at the University of Seville (Gómez-Barea et al., 2011; Gómez-Barea et al., 2013; Nilsson et al., 2012a; Nilsson, 2012). The system is focused on the processing of difficult wastes, whose ash content is high and their nature limits the temperature of the gasifier because of the risk of agglomeration.

6. FLETGAS system

FLETGAS concept

The main lessons learnt from stand-alone, directly-heated, FBG constitute the basis for the development of the new gasification system. The system is represented in Fig. 1.6, showing the main processes taking place in the different parts.

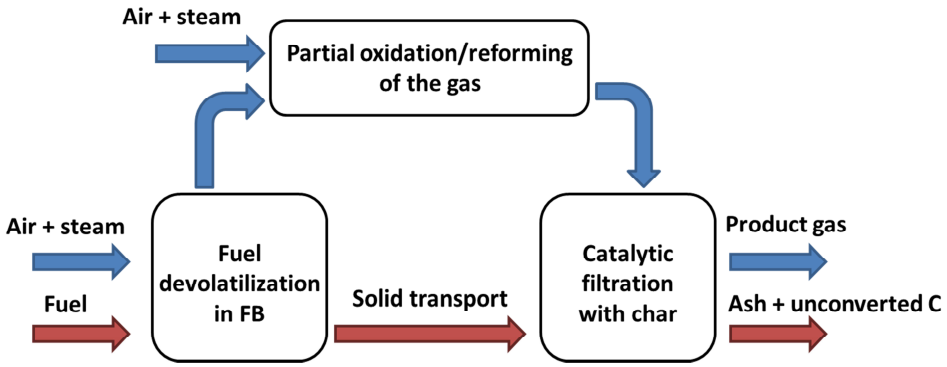


Fig. 1.6. Basis for the conceptual development of the FLETGAS process with indication of the essential steps occurring in various parts of the system.

The three stages contained in the new gasification system are:

- The first stage is a fluidized bed gasifier whose temperature is kept below 800°C. This low temperature makes essentially the first step to be a devolatilizer since negligible char conversion is achieved. Moreover, the gas produced has high tar content. Despite this, the tar is still not aromatized because of the relatively low temperature, so it is expected to be highly reactive. Air and steam are added for fluidization.
- In the second stage, the gas from the devolatilization stage is oxidized/reformed at high temperature in a steam-rich atmosphere. In this zone the highest temperature of the system is achieved by injection of air and steam. Addition of enriched-air (up to 40% of O_2) is also possible since it can be produced at reasonable cost. The maximum temperature is in the order of 1200°C with the aim of achieving high conversion of the tar compounds. At this temperature steam is expected to reform homogeneously the highly reactive tar generated in the first stage. The amount of oxygen injected is determined by the maximum temperature required for the reforming and for the third stage.
- In the last stage, the char generated (the fuel is virtually devolatilized but poorly gasified due to the low temperature of the fluidized bed gasifier) is packed in a downdraft bed serving as a catalyst filter for tar reduction and gas quenching (the endothermic char gasification reactions lower the temperature of this gas as well as of the bed). The benefits of char as catalyst in this third stage is increased

compared to the conventional FBG, i.e. fluidized-bed in a single stage design, because the contact time between char and tar is significantly increased. In this stage the char gasification is promoted by the steam fed in the previous stages. The residence time within the moving bed is determined by the maximum of the following two values: (i) that enabling complete conversion of heavy tars and (ii) that for complete conversion of char. Deactivation of the char has to be considered to correctly predict the residence time of the gas needed for the target conversion.

A gas seal is used to transport the char between the first and the third stages and to conduct the gas produced in the first stage to the second stage. The seal is a fluidized bed that creates sufficient pressure drop to prevent the by-pass of the gas produced in the first stage and to maintain fluidized the solids for the required solids circulation. The fluidization agent is a mixture of air and steam, whose temperature can be adjusted to control the amount of carbon in the char flowing to the third stage and to maintain the thermal balance of the system (the temperatures of the main three stages).

Background of FLETGAS development at US

In order to establish the principle layout of the system, a series of analyses were carried out. Two main challenges are obvious in the development of the concept: (i) to know the optimal operation conditions for a given biomass including the understanding of the tar decomposition under different operation conditions (temperature, steam concentration and residence time) and (ii) the fluid-dynamics of the system (movement of gas and solids from one stage of the system to another). Dried sewage sludge (DSS) was taken as reference fuel for the process development.

The fluid dynamic behavior was studied by means of a cold test rig (Gómez-Barea et al., 2010b). The cold rig was scaled-down from an imaginary $2MW_e$ gasification plant operating with dried sewage sludge following similarity rules of FB (Glicksman et al., 1994). A fluid-dynamic model was developed for this system to theoretically predict the movement of gas and solids, and the distribution of solids between the various sections of the system (Gómez-Barea et al., 2010b).

The conversion behavior of various fuels was studied in experiments with special focus on dried sewage sludge. Devolatilization (Gómez-Barea et al., 2010a) and char gasification (Nilsson et al., 2012b) tests were conducted in a bench-scale rig, which can work in fluidized and fixed bed mode. These results provide the input to a model of the system including the chemical conversion of char and tar. So far a process model has been developed to simulate the system under various conditions (Nilsson et al., 2012a).

Figure 1.7 shows simulation results from a comparison of a single-stage FBG (Gómez-Barea et al., 2008) and the proposed three-stage system using dried sewage sludge. In order to have results which are closer to the available gasifier (Gómez-Barea et al., 2008), the simulation of the single stage FBG was made with a bed temperature of 810°C. The most relevant temperatures calculated in the three-stage system are visualized in Fig. 1.7: 745°C in the bed, 1200°C in the homogeneous reformer and

710°C at the solids' exit. The quench effect is also noted by a temperature drop of 200°C in the moving bed. The efficiency, char and tar conversion in the two systems are indicated below respective gasifier in Figure 1.7. A great improvement is observed, as expected, in the proposed system.

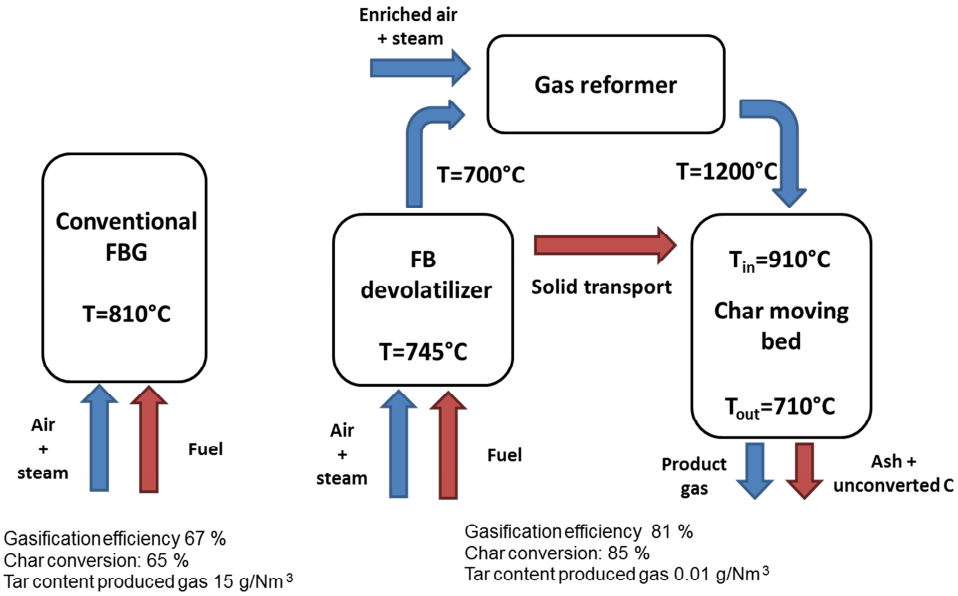


Fig. 1.7. Comparison between a single-stage FBG and a three-stage FBG system (FLETGAS) for sewage sludge gasification.

7. Objective and content of this thesis

The present work extends the studies regarding the FLETGAS process development contained in (Nilsson, 2012) where the fluid dynamic of the system, the devolatilization of different wastes and the char conversion rates were studied. With these experimental data the simulation of the entire system was made to demonstrate the concept as explained above. The results from the present thesis contribute to better assess the performance of the FLETGAS system, particularly to select the operating conditions that optimize the performance regarding the tar concentration and composition (dew point). To achieve that goal, experiments are conducted to provide the necessary knowledge to relate the operating conditions to the concentration and composition of the tar compounds in the gas produced in the various parts of the system.

Two main tasks are developed within this work. The first task aims at studying the influence of operational variables on tar formation and its homogeneous conversion. The specific objectives of this task are: (i) to shed light on the mechanisms of homogeneous conversion of tars and light hydrocarbons and, (ii) to determine the experimental conditions reducing the proportion of heavy tars in the gas during FB

devolatilization. Then this task is intended to provide data to simulate the first stage of the FLETGAS system and, to lesser extent, the second stage. The second task of the work deals with the study of the conversion of aromatic tars over different carbonaceous materials (chars) to simulate the third stage of the FLETGAS system.

Chapter 2 provides information of the experimental rigs, the materials and the analyses and methods applied during the experimental tests. Two different rigs have been used to conduct the experiments. In the first rig a fluidized bed reactor is used for devolatilization tests and the second one is a fixed bed reactor used for studying the tar conversion over char. The system where the gas is prepared before feeding the reactor and that for cleaning the produced gas is common for the two plants (with minor differences). The results obtained from the devolatilization tests (first plant) are presented in Chapters 3 and 4 and those from the second plant (tar conversion over char) in Chapter 5.

In Chapter 3 the influence of the reactor temperature (the same temperature in the bottom, dense zone and in the upper, dilute zone or freeboard) and steam concentration in the carrier gas on the yields of tar and light hydrocarbons generated during devolatilization of died sewage sludge (DSS) in fluidized bed is studied. The temperature is maintained uniform in the reactor aiming at determining the main products of DSS during devolatilization at different temperatures as well as to understand the conversion mechanisms occurring in the process. The range of temperature studied covers that of conventional (one stage) FBG (800-900°C) and also lower temperatures (600-800°C), to investigate the first stage of the FLETGAS system. The investigated range of steam concentration is 0–30 vol%.

Chapter 4 extends the study initiated in Chapter 3 to cover operating conditions of staged FBG and to distinguish between primary and secondary tars. The temperatures of dense bed and freeboard were independently fixed. The primary formation of volatiles was studied varying the dense bed temperature between 500 and 800°C, minimizing their secondary conversion by keeping the freeboard at 600°C. The secondary conversion of volatiles was studied varying the freeboard temperature between 600 and 800°C, while the dense bed was maintained at 500°C. These tests aim at determining the influence on tar composition of staging the feeding of fluidizing agent in the FLETGAS process. The influence of the DSS particle size ranging from 1 to 5 mm is also studied. The composition of the volatiles produced during DSS devolatilization was compared with that using wood pellets in order to establish the influence of the fuel origin.

In Chapter 5 the effectiveness of conversion over three types of char (coal char, coconut char and DSS char) of two aromatic model tars (toluene and naphthalene) is studied at different temperatures (750–950°C) and steam molar fractions (0–25 vol%). The char deactivation process with time is also studied and kinetic expressions for the rate of decomposition of these two tars over the three chars are determined taking into account the deactivation process. The kinetic expressions obtained for the conversion of toluene and naphthalene over DSS char are used for the simulation of the third stage of the FLETGAS system. The previous simulations of the FLETGAS system made in (Nilsson et al., 2012a) using the kinetics of tar conversion over biomass

char from literature (Abu el-Rub et al., 2008) are corrected using the kinetics of the DSS char.

In Chapter 6 the main conclusions extracted from the topics analyzed in this thesis are presented. Recommendations to operate the FLETGAS gasifier with DSS for the production of a gas with minimum dew point are given. Some aspects that need further research are also discussed.

CHAPTER 2

Experimental

1. Introduction

The experiments presented in this thesis were conducted in two different rigs. Both rigs were designed to achieve the particular objectives described below. In the first rig, devolatilization in fluidized bed was investigated. The influence of temperature, steam and temperature stratification along the reactor were varied to study the effect of process variables on tar and light hydrocarbons formation and conversion. The plant was designed to fulfill specific requirements, such as the careful control of gas flow (including steam) and temperature in the various parts of the reactor, as well as the dedicated arrangement for the sampling of both light volatiles and tars. The method for tar analysis itself is also specifically developed for the present work, based on past arrangements and standards (see Appendix 1). The Section 2 of the present chapter gives details of the experimental setup, the fuels used and the analyses conducted. The results are presented in Chapters 3 and 4.

The second rig was specifically designed for the study of tar conversion over char in a laboratory fixed bed reactor. Besides the different reactor used in these tests, the gas feeding and outlet sections used in the devolatilization tests were modified to take into account the specific requirements for these tests. The gas preparation section was modified to handle the further addition of tar and hydrogen to the incoming gas. Since the interest was focused on the tar conversion rate over a char bed and its evolution with time, the experimental setup was designed to allow discontinuous tar sampling during test time. Information about the experimental setup and the materials used during these tests is presented in Section 3 of the present chapter. The results are discussed in Chapter 5.

Besides the above information, the analyses made to characterize the fuels and samples are also described. The methods for tar sampling and analysis have been discussed in detail in Appendix 1.

2. Experiments of devolatilization in FB

This section summarizes the experimental setup used during the study of the influence of the different parameters affecting the formation of light gases and tar compounds during the devolatilization of biomass and waste in FB.

2.1. Fuel

The fuels used were dried anaerobically digested sewage sludge (DSS) granulates and commercial wood pellets. The ultimate and proximate analyses and the corresponding ASTM and UNE-CEN/TS standards are given in Table 2.1.

Table 2.1. Ultimate and proximate analysis of the tested fuels

	DSS			Wood pellets		
	Wet basis	Dry basis	Dry and ash free basis	Wet basis	Dry basis	Dry and ash free basis
LHV (MJ/kg)	-	12.47	21.94	-	18.39	18.52
HHV (MJ/kg)	-	13.41	23.59	-	19.65	19.79
C* (wt.%)	-	30.88	54.34	-	49.47	49.96
H* (wt.%)	-	4.36	7.67	-	5.79	5.84
N* (wt.%)	-	4.76	8.38	-	2.03	2.05
S** (wt.%)	-	1.24	2.18	-	0.06	0.06
O (wt.%)	-	15.61	27.47	-	41.94	42.36
Moisture^{+} (wt.%)	0.65	-	-	1.03	-	-
Ash^{++} (wt.%)	42.87	43.15	-	0.70	0.71	-
Volatiles^{X} (wt.%)	51.41	51.75	91.08	80.15	80.98	81.79
Fixed C (wt.%)	5.07	5.10	8.98	18.12	18.31	18.49

*: UNE-CEN/TS 11510 EX
**: ASTM D4239
+: UNE-CEN/TS 14774-1 EX
++: UNE-CEN/TS 14775 EX
X: UNE-CEN/TS 15148 EX

The DSS was received in the form of spherical granulates with 98 wt.% in the range of 2−4 mm. Before its use the DSS granulates were sieved into three different size ranges, 1−1.4 mm, 2−2.8 mm and 4−5 mm. In most tests the size range used was 2−2.8 mm. However in the tests studying the influence of the particle size the three size ranges were employed. The particle density of DSS was 1400 kg/m^3. Cylindrically−shaped wood pellets were used to compare the results obtained using DSS with those with this widely studied fuel. Wood pellets had 6 mm of diameter and a length ranging from 8

to 12 mm, with a particle density of 1300 kg/m^3. Both fuels were dried for 16 hours at 105°C and stored in a dry atmosphere before being used.

2.2. The rig

A fluidized bed laboratory reactor was designed and constructed. The main components of the reactor system are presented in Fig. 2.1. The main parts of the system are described in detail below.

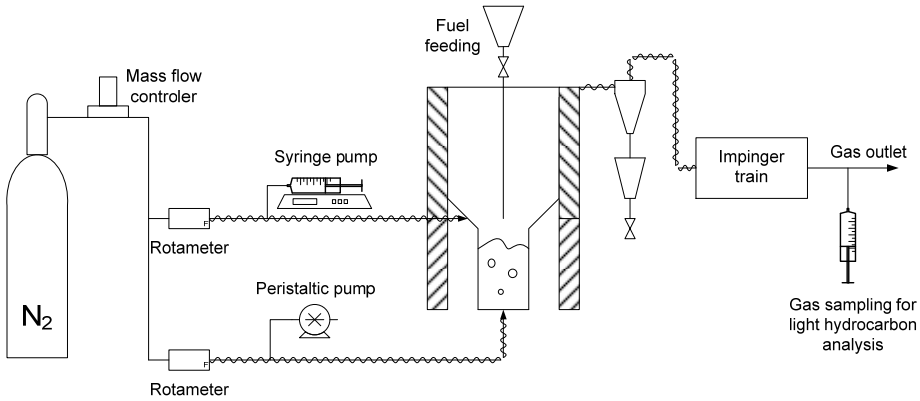


Fig. 2.1. Schematic diagram of the experimental rig.

2.2.1. Fluidizing agent feeding system

The nitrogen flow was controlled by means of a mass flow controller placed after the N_2 bottle. Before the heating of the nitrogen, this stream was divided in two in order to adjust the residence time required (specified) in the two zones of the fluidized bed: bottom zone and freeboard (see Figure 2.2). The main stream fed the system at the bottom of the reactor, passing through a windbox (plenum) and distributor (plate with orifices). A second line transports the nitrogen to the port situated in the conical transition zone, between the bottom zone and the freeboard (Figure 2.2). The flowrate of the two streams of nitrogen was controlled by means of two rotameters.

After the division, both streams were heated by heat tracing surrounding the lines. In the tests with steam injection, liquid water was fed with a peristaltic pump to the bottom zone line and with a syringe pump to the transition zone line. The fluidizing agent (N_2 or mixtures of N_2/steam) was heated to establish the temperature of the gas entering the reactor at 350°C.

The flowrate of fluidizing agent was calculated for every test condition to set a given (prefixed) gas residence time in both the bottom zone and the freeboard. The gas residence time in the bottom zone was fixed at 0.6 s and the gas residence time in the upper zone (freeboard plus transition zone) was 1 s in all tests. The gas residence time was calculated based on superficial velocity of the nitrogen, i.e. by dividing the flowrate of nitrogen by the empty section of the reactor. Therefore the small contribution of the volatiles released from the fuel was neglected.

2.2.2. Fluidized bed reactor

The FB reactor is made of refractory steel AISI 310. Fig. 2.2 illustrates its different parts. It is divided in two zones, a bottom part with an internal diameter of 53 mm and height of 192 mm, and a freeboard with internal diameter of 81 mm and height of 165 mm. A conical transition zone with height of 50 mm connects the bottom and freeboard parts. The inert bed material used was bauxite (aluminosilicate) with particle size between 250 and 500 µm, having a minimum fluidization velocity of 0.20 m/s (Nilsson, 2012). The static bed height was 80 mm (300 g of bauxite) and the gas velocity in the bottom zone was kept constant at 0.31 m/s. Fig. 2.2 illustrates the internal zone occupied by bed material (dense zone) as well as the space where the gas flows upward in a dilute (almost free of particles) phase.

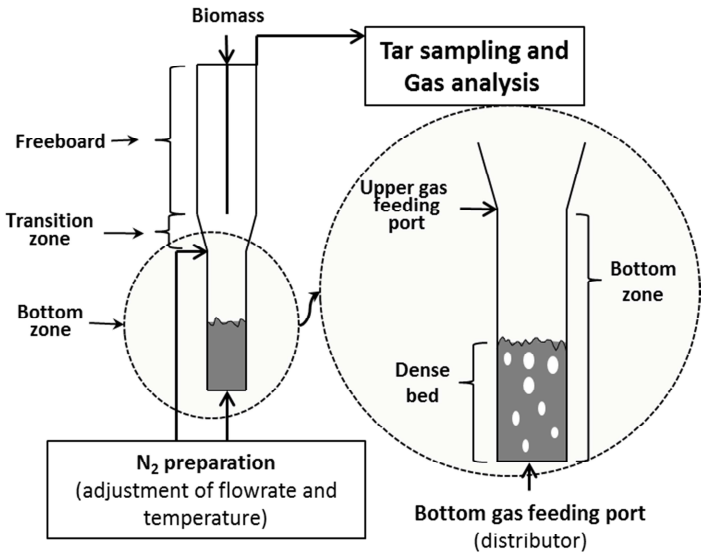


Fig. 2.2. FB reactor

The reactor was heated by an external electrical oven of 10 KW_e allowing for independent temperature control of bottom and freeboard zones. The temperature of the bottom zone of the reactor was controlled by means of a thermocouple inserted at 40 mm of the distributor (immersed in the dense bed of bauxite) and connected to the furnace controller. The thermocouple controlling the upper zone of the furnace (freeboard temperature) was inserted at 377 mm of the distributor and 30 mm under the gas outlet.

The fuel feeding system consisted of two hoppers separated by two ball valves. The lower ball valve connected the second hopper with the stainless steel discharge tube. The fuel fell through the discharge tube by gravity to the dense bed. The interaction between the fuel and the gas in the freeboard was prevented because the end of the discharge tube reaches the transition zone (just above the bottom part of the reactor).

2.2.3. Exit line and sampling ports

The exit line, from the reactor outlet to the tar sampling train, was traced and isolated to maintain the product gas at 330°C. This temperature prevents tar condensation inside the pipes. Between the reactor and the tar sampling train a cyclone was installed to reduce the solids load reaching the tar sampling train. However, since no other particle filter was installed, it was unavoidable that some fine solids reached the first impinger of the tar sampling train, making the solvent filtration necessary before tar analysis (see Appendix 1).

The tar sampling train had 7 impingers filled with isopropanol at -20°C, 4 of which having glass frits to improve the contact between liquid and gas. All the gas from the reactor passed through the tar sampling train, where heavy organic compounds are condensed. The visual inspection of the two last impingers after sampling showed that the solvent was colorless in all cases, indicating that most heavy tars and smog formed were captured. The solvent was recovered after each test and the train was washed with acetone. Both solvents (isopropanol from the impingers and acetone from the washing) were mixed and stored at -20°C.

The light gas was discontinuously sampled during the fuel devolatilization every few seconds using 5 gas-tight syringes. The gas sampling port consisted in a rubber septum placed in the exit line after the tar sampling train. This location was selected in order to avoid the presence of tars in the gas sample, which could deteriorate the sampling syringes and the micro-GC during the light gas analysis.

2.3. Product analysis

2.3.1. Light gas compounds

The gas samples were analyzed using a micro-GC model 3000A (Agilent) with 2 channels. The channel A, with a plot U/MS capillary column, measures the concentration of H_2, O_2, N_2, CO and CH_4. The channel B, with a Plot U/U capillary column, measures the concentration of CO_2, C_2H_6, C_2H_4, C_2H_2 and C_3H_8 + C_3H_6 (both in one peak). The time employed for each analysis by the micro-GC is between three and four minutes.

The procedure used to calculate the overall yield of the different light gas species is explained as follows. During the devolatilization stage the gas was discontinuously sampled every few seconds using 5 gas-tight syringes (see Fig. 2.1). Devolatilization lasts between 60 and 120 seconds, depending on the test temperature. Since each operation condition was repeated at least 2 times, at least 10 gas samples were taken for every operation condition (5 samples in each test). The evolution with time of the individual yields was obtained by fitting the measurements (comprising 10 or more points) to a continuous function. The total (accumulated) yield of each gaseous species was calculated by integration of the curve. Some of these samples were found to contain oxygen. In this case the concentration of the different gases was re-calculated assuming that the source of oxygen was air (N_2/O_2 in proportion of 79/21 vol/vol), contained in the sample due to a leaking syringe. Fig. 2.3 presents an example of the

measured concentration of one species in the gas and the curve resulting from the fitting. The points correspond to the measurements obtained at different times during two tests under the same operating conditions.

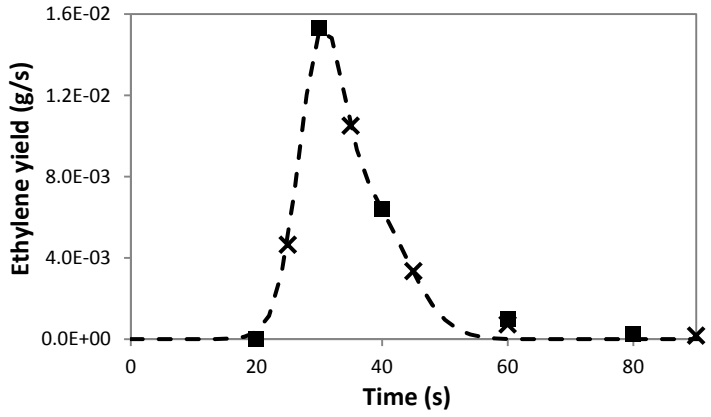


Fig. 2.3. Example of determination of light gas compound (ethylene). Experimental yield (markers) and fitting (dashed line) of ethylene at 900°C without steam addition. The total yield of ethylene calculated was 70 mg/g daf fuel. The two types of markers represent the measurements taken in two tests conducted under the same operation conditions.

2.3.2. Tar compounds

Three different techniques were used to characterize the tars produced during the devolatilization tests: (1) gas chromatography-mass spectrometry (GC-MS) for determination of aromatic tars from benzene to perylene; (2) solvent distillation for gravimetric tar determination; and (3) elemental analysis of the gravimetric residue. This section presents the main aspects of the analysis conducted, further details of the analytical procedure can be found in Appendix 1.

The GC-MS analysis method for aromatics quantification was applied following the method described in (Rochembach, 2001). Identification and quantification of aromatics were performed using a gas chromatograph Agilent mod. 6890N coupled to a mass spectrometer Micromass Autospec-Q equipped with an electronic impact (EI) ionisation source (GC-EI-MS). GC analyses were performed on a 60 m x 0.25 mm i.d., 0.25 μm film thickness TRB-Meta X5. Mass spectra were obtained in *Scan* mode, in a range of 30-650 amu, to preliminarily identify the different tar molecules present in the samples, allowing for quantification of low weight or non-polar components. However it was not possible to quantify components with high polarities, arising in significant quantity at low temperature (Evans and Milne, 1987), because they are irreversibly retained in the GC column.

The aromatic tars analyzed by GC-MS were lumped into families or groups using the classification described in (van Paasen, 2004). This classification divides the tar

compounds according with their behavior in downstream processes, making it a useful tool for the assessment of the quality of the gas for a given application. This classification was chosen instead of that presented in Chapter 1 (Evans et al., 1998) because the latter is focused on the grouping of tar compounds according to the severity conditions applied during generation (temperature and time). Then the classification of Evans is oriented to distinguish between tars that have been generated through different chemical transformations. Table 2.2 summarizes the tar lumping according with both classifications.

Table 2.2: Tar classification according with (van Paasen, 2004) and (Evans et al., 1998).

Classification by (van Paasen, 2004)	
Tar class	**Description**
Tar class 1	Undetectable by GC analysis*
Tar class 2	Heterocyclic aromatics
Tar class 3	One ring aromatics
Tar class 4	Light polyaromatics (2-3 rings)
Tar class 5	Heavy polyaromatics (4-7 rings)

Classification by (Evans et al., 1998)	
Tar class	**Description**
Primary	Parent fuel fragments
Secondary	Alkyl phenols and olefins
Alkyl-tertiary	Alkyl-aromatics
Condensed-tertiary	PAH

*using a column for aromatics determination (non-polar)

Gravimetric analysis gives a rough indication of the tar compounds in the mixture that would condense at ambient temperature. The sampling method (CEN/TS 15439, 2006) comprises a cold impinger train filled with an organic solvent (isopropanol in our case) where the condensable volatiles are captured. Vacuum distillation in a rotary evaporator at 1,5 KPa and 55°C was applied to the tar samples until constant weight was achieved. Despite the simplicity of the gravimetric method, a significant part of light organic compounds such as benzene escapes from the sample and inorganic salts such as ammonium chloride are found in the solid residue (Timmerer et al., 2007). Hence gravimetric samples mainly contain tars with a high molecular weight, such as primary heteroatomic compounds or PAH (depending on the temperature of the test), and inorganic salts.

The quantification of carbon, hydrogen, nitrogen and sulfur in the gravimetric residue (after vacuum distillation described above) was carried out with an elemental analyzer LECO CHNS 932. The oxygen concentration is determined by difference assuming no other elements in the sample.

In the analysis of results presented in Chapters 3 and 4 different tar fractions have been defined based on the tar analysis methods employed. Gravimetric tars and GC

tars are the direct results of the methods described above. The classes of tars (2 to 5) follow the classification from (van Paasen, 2004): Tar class 2 are heterocyclic compounds (mainly phenols) with high water solubility, Tar class 3 includes one-ring aromatic hydrocarbons (also named in the following light aromatic hydrocarbons, LAH) and Tar class 4 (2-3 aromatic rings) and 5 (4-7 aromatic rings), are, respectively, light and heavy polyaromatic hydrocarbons (LPAH and HPAH). The GC-undetectable tar fraction comprises all tars whose concentration cannot be measured by the GC-MS method. This fraction contains tars with a high polarity and tars with a high molecular mass, which are irreversibly retained in the GC column used. The aromatic non-volatile tars (ANVT) is defined as the sum of all tars measured by GC-MS minus the BTXs (Benzene + Toluene + Xylenes). This fraction is composed by the aromatic tars analyzed by GC-MS which remaining in the gravimetric tar residue after vacuum distillation (BTX are mainly lost with the solvent due to their high volatility).

2.4. Scalability of the results from FB devolatilization

The conditions under which the fuel is devolatilized in a small batchwise operated laboratory FB such as the one used here differs from those in commercial FB gasifiers. In the latter oxygen is part of the fluidization agent, there is a continuous feeding of biomass and no external heating is applied. In addition, the larger size of an industrial FB gasifier induces gulfstream, making the rates of solid and gas mixing different from that in a small FB. These issues have to be considered in order to establish the way in which the results obtained in such a laboratory device could be used in larger FBG and, for the particular objectives of the present thesis, to the FLETGAS gasifier. The main considerations addressing these issues are summarized below and detailed explanations are presented in Chapters 3 and 4 during discussion of the results.

The extent of solids and gas mixing in the FB significantly influences the rate of devolatilization and the yields of the volatiles released from the particles (Gómez-Barea & Leckner 2010). The position where a fuel particle is converted depends on the rates of vertical and horizontal mixing and on the position of the fuel feeding port. This issue is significant in commercial plants where the position at which the particle is devolatilized can influence the final composition of the gas. In large commercial units the oxygen concentration decays with the bed height and, in consequence, the interaction volatiles-oxygen is lower at the bed surface. In addition the volatiles released from fuel particles at the bottom of the dense bed interact deeply with the bed material (which could be a catalyst). However, as it was commented in Chapter 1, during devolatilization most of the fuel particles are at the bed surface due to their inherent floatability (Gomez-Barea & Leckner, 2010). As a result, the interaction of volatiles with oxygen and bed material is limited in commercial FBG. In addition, the influence of the composition of the surrounding gas on the distribution of products during devolatilization of DSS particles was found to be small (Nilsson, 2012). In consequence, the tar conversion process is mainly driven by the temperature profile of the gasifier, influencing the gas composition only at the freeboard, where secondary reactions of volatiles occur. It is concluded that the tar conversion process in FBG would be well reproduced in laboratory tests in the absence of oxygen.

In the tests conducted in Chapters 3 and 4 the gas velocity chosen was close to that of minimum fluidization, so the dense bed is expected to be only slightly expanded and stirred. Hence, the extent of fuel-dense bed mixing should be small (particles are in the upper part of the dense bed during devolatilization) reducing the interaction between the volatiles and the dense bed. In commercial FBG if the gas velocity is higher and the gulfstream pattern tends to take the particles down and devolatilization also occurs partially in the internal part of the dense zone. In this case the application of the results obtained here could be questionable.

The heating rate of the fuel particles is similar in commercial FBG and in the laboratory rig. On the one hand the heat transfer coefficient is hardly affected by the gas velocity because the fuel particles are converted in the emulsion where the flow conditions are close to that of minimum fluidization (the gas in excess pass in the form of bubbles). On the other hand, the mixing and uniform temperature in an industrial FB is achieved by using high gas velocity, since the bubbles are the stirring mechanism in the bed. In the present tests, the uniform temperature was achieved at the low gas velocities by keeping low the mass ratio between the fuel and the bed material and by uniform distribution of the heat flux in the oven.

3. Experiments of tar conversion over fixed bed of char

In this section the experimental setup used during the tests studying the conversion of tar over fixed bed using various chars is presented. Some of the components of the setup are the same as those described in the previous section but other components (reactor, gas exit line,…) have been modified aiming at addressing the particular objectives of these tests. The main objective of these tests is to assess the capability of chars for tar conversion in fixed-moving beds studying the influence of temperature, steam concentration and the internal structure of the char. Various chars representing different internal structures and two model tars, both aromatics, representing a high temperature tar mixture were used.

3.1. Material

3.1.1. Chars

Three different chars were employed, two commercially available and one prepared in our facilities. The commercial chars were coconut char (irregularly shaped particles) and coal char (flaked particles) with particle size in the range of 1–2.8 mm. The third char was generated by pyrolyzing dried sewage sludge (DSS) granulates at 900°C in a laboratory oven. The method for char preparation has a great influence on its gasification reactivity (Nilsson et al., 2012b), underlining the significance of the thermal history of the char used. Therefore aiming at simulating the real conditions in the third stage of the FLETGAS process (described in Chapter 1) the chars studied should have been generated in FB conditions and tested without cooling down. However, this procedure was not possible to be applied in our experimental rig so the char preparation method is one of the main limitations in the present study. The

effects of the previous cooling of the char over the reactivity in tar conversion should be tested in future work.

The DSS char was sieved to particle size between 2 and 2.8 mm. The char was heated and kept at 105°C for 16 hours and then stored in a dry atmosphere before being used in the tests. The proximate and ultimate analyses as well as the bulk density of the three chars are presented in Table 2.3. The negative value for oxygen content and the high carbon content in the ultimate analysis of DSS char are explained by the presence of carbonates in DSS ashes. These carbonates decompose during the combustion of the sample in the ultimate analysis but they do not decompose during combustion in the proximate analysis due to the lower temperature applied in the latter. Hence the CO_2 produced during the carbonates decomposition is detected during the ultimate analysis and quantified. Therefore it could be assumed that the "organic" carbon is close to that quantified by the proximate analysis (12.0%).

Table 2.3. Chemical analysis and bulk density for the three chars tested and that for commercial biomass char presented in (Abu el-Rub et al., 2008).

	Coconut char	**Coal char**	**DSS char**	**Commercial biomass char**
Proximate analysis (% dry basis)				
Volatiles	2.6	3.9	3.2	-
Ash	5.8	2.2	84.8	9.55
Fixed carbon (by diff.)	91.6	93.9	12.0	-
Ultimate analysis (% dry basis)				
C	91.4	94.0	18.1	89.03
H	0.3	0.6	0.5	0.12
N	0.9	0.6	1.1	0.24
S	<0.05	<0.05	0.8	-
O (by diff.)	1.7	2.6	-5.2	1.06
Bulk density (Kg/m^3)	530	164	575	520
Particle size range (mm)	1-2.8	1-2.8	2-2.8	1.4-1.7

The selected chars were chosen aiming at studying three materials with very different internal structures. Table 2.4 shows various measurements characterizing the internal structure of the chars. Coconut char has the lowest porosity and the largest micropore surface area, whereas char from coal has the largest porosity, total surface area, and macropore volume. DSS char presents the lowest total surface area, having most of the pore volume as macropore. Methods used for internal structure measurements are described in Section 3.3.3.

Table 2.4. Properties characterizing the internal structure of the three fresh chars (before the tests).

	Total surface area (BET) (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Macropore volume (cm^3/g)	Porosity (%)
Coconut char	597	482	0.27	0.08	0.08	16.9
Coal char	635	375	0.21	0.21	2.26	73.7
DSS char	55	17	0.01	0.07	0.46	53.4

3.1.2. Silicon carbide (CSi)

Silicon carbide was used as non-porous reference material to compare its activity for tar decomposition with the three chars investigated. Silicon carbide particles were sieved between 2 and 2.8 mm.

3.1.3. Tar compounds

Two tar compounds, toluene and naphthalene, were selected as model tars. Toluene and naphthalene were mixed to prepare a liquid tar mixture in the proportion 60/40 wt% (toluene/naphthalene). The amount of tar injected in the gas was adjusted to give a tar concentration within the typical range for biomass gasification gas. Details about the operating conditions are given below.

The reason for the choice of these two compounds is that naphthalene is the lightest PAH, whereas toluene is the lightest alkyl-aromatic tar, so their rates of decomposition over char are expected to be the lowest of each corresponding tar group (PAH and alkyl-aromatics) as will be discussed in Chapter 5 (the activity increases with molecular weight for a given family/type of tar).

3.2. The rig

A fixed bed laboratory reactor was designed and constructed for conducting the tests of tar conversion over char beds. The main components on the reactor system are presented in Fig. 2.4.

3.2.1. Gas and tar feeding system

Nitrogen and hydrogen were used as carrier gases in tar conversion over char tests. The gas flow of both gases (N_2 and H_2) were adjusted by means of two mass flow controllers. H_2 was added to the gas to take into account its effect on char gasification (Matsuhara et al., 2010; Bayarsaikhan et al., 2006) and its concentration was fixed at 8 vol% to simulate a typical hydrogen concentration in conventional FBG. The gas mixture was heated up to 400°C and then, water and tars were fed to the carrier gas by a peristaltic pump and a syringe pump, respectively (see Fig. 2.4).

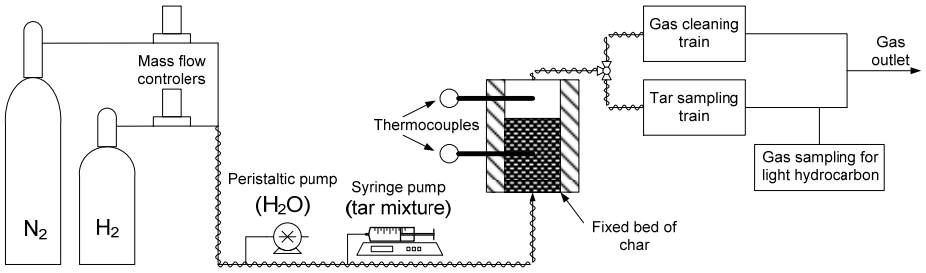


Fig. 2.4. Layout of the experimental plant

3.2.2. Fixed bed reactor

The laboratory fixed bed reactor is a stainless steel AISI 316 tube with 53 mm of internal diameter. A metallic grid situated at the bottom of the reactor supported the coarse particles forming the fixed bed. The reactor was filled with a 100 mm tall char bed for all the tests. The mass of char bed depends on the type of char, given by its bulk density (see Table 2.3).

The temperature of the bed was controlled by a K-type thermocouple situated near the center of the bed, which was connected to the furnace controller that adjusted the heat to the reactor. A second K-type thermocouple was situated at the exit of the char bed to verify that the temperature of the gas leaving the bed was close to that in the bed. It was found that the difference between temperature measurements was always within ±5°C.

3.2.3. Exit line and sampling ports

Downstream of the reactor the gas flows through one of the following two alternative lines. The first one comprises a cleaning system composed by four bottles filled with oils and solvents at 0°C. This line was used during most of test duration for tar removal before the gas emission. When samples of tar and gas were taken the gas was directed to the second line, which comprises the sampling trains for measuring tar and gas composition. Both lines were isolated (trace heating was found to be unnecessary) to maintain the product gas at temperature above 350°C, preventing tar condensation inside the pipes.

Tar and light gas sampling were conducted with the same devices as those presented in Section 2.2.3.

3.3. Product analysis

This section summarizes the analysis conducted to characterize the light gas, tar and char samples taking during the tests studying the tar conversion over chars.

3.3.1. Light gas compounds

During each tar sampling period two gas samples were taken by using gas-tight syringes and analyzed by micro-GC (model 3000A Agilent). The content of H_2, CO, CO_2 and CH_4 in the gas was determined. As was mentioned before heavier hydrocarbons (C2 and C3 species) can also be measured with the micro-GC device but no significant concentrations were detected in these tests.

3.3.2. Tar compounds

The solvents (isopropanol from the impingers and acetone from the train washing) recovered after each tar sampling was analyzed by GC-MS for the quantification of the model tars (toluene and naphthalene).

3.3.3. Char porosity

The internal structure of chars was analyzed both before (fresh char, see Table 2.4) and after the tests (spent char, to be presented in results of Chapter 5). Two experimental techniques were applied: gas adsorption and mercury intrusion porosimetry. Gas adsorption measurements were performed at -196°C in a Micromeritics ASAP 2020. The isotherms were analyzed by BET method for the total surface area and by t-plot method for micropore surface area and micropore volume. The mercury intrusion porosimetry was performed in a Micromeritics Autopore IV. This technique allows determination of macro and mesopore volumes and the total porosity of the char samples (neglecting the micropore volume).

3.4. Data treatment

From the experimental results of $C_{tar,in}$ and $C_{tar,out}$ (inlet and outlet tar concentrations respectively) the tar conversion, χ, in the char bed was calculated at different times of exposure to the gas stream.

$$\chi = \frac{(C_{tar,in} - C_{tar,out})}{C_{tar,in}} \tag{2.1}$$

The tar conversions, χ, calculated from Eq. (2.1) were fitted to a continuous function to estimate χ at different times from 5 to 75 minutes. This fitting was made in order to reduce the dispersion of the experimental data and to increase the number of measurements for the kinetic modeling. Fig. 2.5 presents the tar (toluene) conversion measurements and fitting curves for one char (DSS char) at three different temperatures.

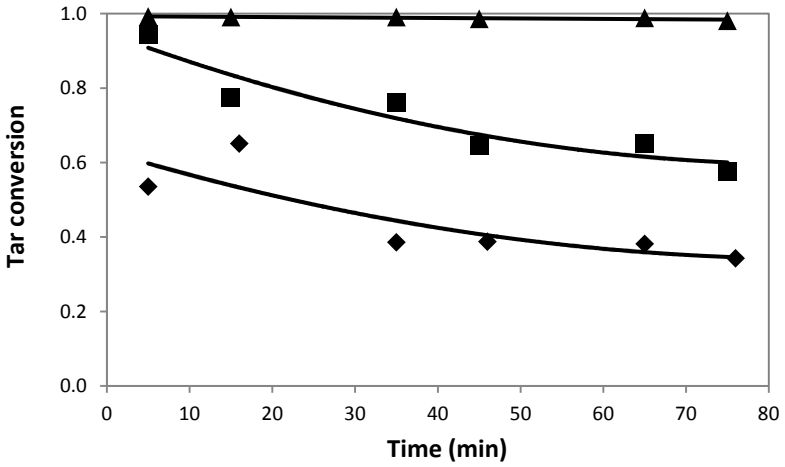


Fig. 2.5. Tar (toluene) conversion over char (DSS char) at different times. Markers belong to experimental data and lines belong to the fitting. ▲: 950°C, ■: 850°C and ◆: 750°C.

4. Summary

Two experimental plants were designed and constructed to study different aspects of fuel devolatilization and volatile conversion in fluidized bed and tar conversion over char. This chapter describes the main components of the two plants employed in this thesis to conduct the experiments, including the materials used and the procedures applied during the analysis. Both plants were designed to obtain dedicated data for the development of the various key stages of the FLETGAS system, described in Chapter 1.

The results from the devolatilization tests in the fluidized bed plant are presented in Chapter 3 and 4. In Chapter 3 the influence of homogeneous temperature and steam on volatiles (mainly focused on tars and light hydrocarbons) is studied. In Chapter 4 the influence of the particle size and the temperature of formation and secondary conversion on tar and light hydrocarbons is investigated. Results from the tests conducted in the second plant (a fixed bed reactor) are presented in Chapter 5. This plant was designed to study the activity of various chars for tar conversion and their deactivation with time.

CHAPTER 3

Influence of reactor temperature and steam concentration on the products of devolatilization in a fluidized bed

The influence of temperature and steam concentration in the gas on the yields of tar and light hydrocarbon compounds generated during devolatilization of dried sewage sludge in a laboratory fluidized bed reactor is investigated in this chapter. The temperature is maintained uniform along the reactor in order to determine the main tar compounds generated at different temperatures as well as to investigate the conversion mechanisms in conventional FBG (with roughly uniform temperature). The influence of the steam concentration in the gas on the devolatilization products and its role in the reforming reactions of tars and light hydrocarbons are also studied.

The results from this and the next chapter (where further effects are considered) give a fundamental basis for understanding the expected distribution of volatiles in the gas from the first stage of the FLETGAS gasifier under different operational conditions, and in turn, enabling the optimization of the system for significant reduction of heavy tars in the produced gas to lower the gas dew point to the extent needed for burning it in a gas engine.

1. Introduction

Devolatilization is a key stage during gasification and other fuel conversion processes. During gasification of a fuel containing high proportion of volatile matter, such a biomass or waste, the produced syngas is mainly characterized by the volatiles generated during devolatilization (Gómez-Barea & Leckner, 2009). The gas composition of the produced gas is strongly linked to: 1- the conditions at which the

fuel is devolatilized (mainly temperature and heating rate) and 2- to the conditions that the volatiles meet once they are released from the fuel particle (temperature, presence of reactive substances, catalysts, etc.).

The devolatilization process in FB gasifiers is produced at high heating rates and temperatures in the range of 700-900°C (dense bed temperature). Once released form the particle, the tar compounds interact with the bed material and other gaseous species such as steam, other volatile compound and/or oxygen. However, as was discussed in the Chapter 1, 1- most oxygen is consumed within the dense bed, 2- most devolatilizing particles tend to float on the surface of the dense bed and 3- light gases are oxidized faster than tar. Hence the interaction tar-oxygen is not expected to be the main mechanisms for tar conversion in an FBG.

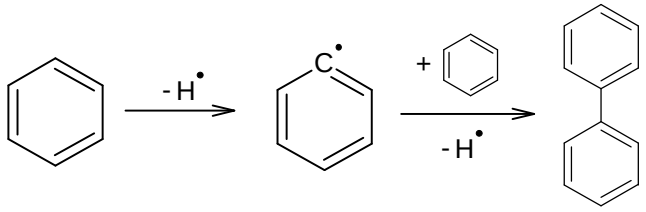
Tar formation and conversion have been widely studied in the last decades (Morf et al., 2002; Stiles & Kandiyoti, 1989; Jess, 1996; Marsh et al., 2004; Wornat & Ledesma, 2001; Ledesma et al., 2002a; Ledesma et al., 2002b; Li & Nelson, 1996; Williams & Taylor, 1993; Taralas et al., 2003; Fagbemi et al., 2001; Xu & Tomita, 1989). Two different kinds of experiments have been carried out. In the first type a model tar is converted in a controlled atmosphere, allowing for tracking the decomposition process and the determination of the conversion kinetics (Jess, 1996; Marsh et al., 2004; Wornat & Ledesma, 2001; Ledesma et al., 2002a; Ledesma et al., 2002b). In the second type of tests the production and conversion of tar compounds generated from fuel decomposition are studied. This method is complex but enables determination of more realistic tar formation-conversion reactivity. However, due to the large number of compounds in the gas, it is difficult to accurately determine the reaction scheme and interaction between tar compounds and bulk gas.

Fig. 3.1 presents a review of the main conversion mechanisms during thermal conversion of aromatic tars reported in literature. The first (Morf et al., 2002; van Paasen, 2004; Cypres, 1987; Bruinsma & Moulijn, 1988; Ledesma et al., 2000; Lu & Mulholland, 2004) and the second (Morf et al., 2002; Ledesma et al., 2000; Thomas et al., 2007) mechanism increases the molecular weight of the product tar. These two mechanisms are the main source of PAH and soot in the product gas of an FBG. Both mechanisms are essentially the same; a sequence of H abstraction from the aromatic structure followed by the addition of one compound (the first stage activates the molecule that further grows, converting it into a radical), being the nature of the compound added the only difference. The third mechanism (Jess, 1996; Ledesma et al., 2002a; Taralas et al., 2003) leads to the increase in the aromaticity of the tar mixture by the cleavage of alkyl groups attached to aromatic rings. The fourth mechanism is the decarboxilation of phenolic compounds to form cyclopentadiene-derivates and CO. Cyclopentadiene-derivates may either further react to produce high molecular weight tars by dimerization (Morf et al., 2002; Cypres, 1987; Sharma & Hajaligol, 2003) or to decompose into low molecular weight hydrocarbons (Ledesma et al., 2002a; Scheer et al., 2010; Scheer et al., 2011).

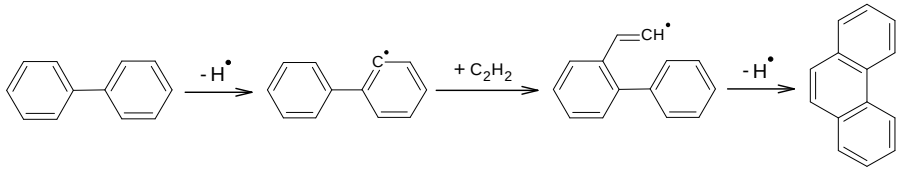
The presence of light hydrocarbons in the gas mixture, such as acetylene or propene, influences the tar transformations as shown in Figure 3.1 (Mechanism 2). These compounds, light unsaturated hydrocarbons, may also produce aromatic compounds

at high temperature via Diels Alder reactions followed by a dehydrogenation stage (Ledesma et al., 2002a; Williams & Taylor, 1993; Horne & Williams, 1996). Therefore, due to the strong interaction between light hydrocarbons and aromatic compounds, the studies focused on tar formation and conversion should report the concentration of the former compounds.

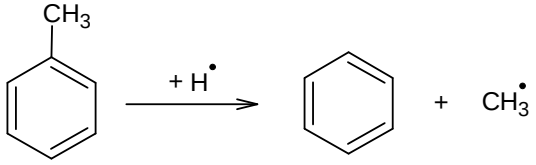
1- Dimerization



2- Light unsaturated hydrocarbon addition to aromatic structures



3- Dealkylation



4- Decarboxilation of phenolic compounds

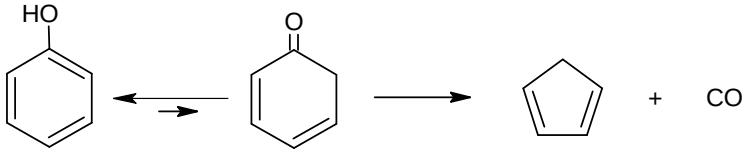


Fig. 3.1. Mechanisms involved during thermal conversion of aromatic tars.

It has been found that during thermal conversion of gas mixtures containing aromatic tars, the presence of steam neither modifies the tar yields (Zhang et al., 2010) nor the rate of tar reactions (Jess, 1996; Miura et al., 2003), as far as no catalyst is used and the temperature is below 1100°C (Jess, 1996). Moderate reduction in the yields of pyrolysis tars, mainly non-aromatic or alkyl-aromatic compounds, has been reported when steam concentration is increased (Zhang et al., 2010; Jönsson, 1985; Wang et al., 2009). Furthermore, the addition of steam to the reacting mixture has been found to decrease the yield of soot, due to the enhancement of the rate of soot gasification at higher steam concentration (Zhang et al., 2010; Miura et al., 2003; Wang et al., 2009).

The adjustment of operating conditions in FBG is made by changing the flowrate of fuel and gasification agent, as well as the composition of the latter. This adjustment aims at setting the desired reactor temperature and, consequently, influences the composition of the outlet gas. To evaluate the necessary measures to optimize gas composition, the influence of the operating conditions on the quality of the gas product (mainly tar composition and concentration) has to be known. Two easily affordable measures in conventional FBG are the adjustment of the reactor temperature (by modifying the stoichiometric ratio SR, also called equivalence ratio) and the addition of steam to the fluidizing agent. The influence of these measures on the yields of specific tar and light hydrocarbons has to be known prior to the adoption of any of them. The composition of the tar mixture, rather than the total tar concentration, is the key factor in applications such as power generation in gas engines, where equipment may be affected by tar condensation (Kiel, 2004). Since the presence of heavy tars (especially heavy polyaromatic hydrocarbons, HPAH) mainly defines the dew point of the gas, the understanding of the conditions under which these compounds are generated is critical in these devices.

In the present chapter the influence of temperature and steam concentration on individual yields of tar and light hydrocarbon compounds during devolatilization of batches of dried sewage sludge in a fluidized bed reactor was investigated. In Chapter 4 the work is extended to investigate the effects of other measures influencing the tar and light hydrocarbon composition in staged gasifiers, such as the staging of the gasification agent to yield various thermal levels in the gasifier. Thus, in Chapter 4 the effects of different temperature in the dense bed and freeboard on the composition of primary and secondary volatiles are investigated. The influence of the particle size and comparison of DSS with wood are also studied in Chapter 4.

Tests were conducted at temperatures in the range of 600-900°C. This temperature level is within the range in which conventional FBG operate (800-900°C) and also includes lower temperatures that are, maybe, interesting to adopt in the first stage of the FLETGAS system. Temperatures above 900°C were not considered practical because of the risk of agglomeration (Gómez-Barea & Leckner, 2010) when using waste and other difficult fuels. The fuel chosen was dried sewage sludge (DSS) because gasification may be an interesting alternative to valorize this residue (Mun et al., 2009; Aznar et al., 2008; Adegoroye et al., 2004; van Paasen et al., 2006) compared to more conventional processes (Werther & Ogada, 1999).

2. Experimental procedure

The experimental conditions tested are summarized in Table 3.1. Tests were conducted at temperatures between 600°C and 900°C and steam concentrations of 0% and 30%. The residence time in the reactor was fixed at 1.6 s, 0.6 s for the bottom zone and 1 s for the freeboard (see section 2 in Chapter 2). The gas residence time was calculated on the basis of superficial velocity of the fluidizing agent, i.e. by dividing the flowrate of fluidizing agent by the empty section of the reactor neglecting the contribution of the volatiles. To maintain these residence times the flowrate of fluidizing agent was adjusted for each temperature.

Table 3.1. Summary of experimental conditions. In all tests the mass fed of dry DSS was 5 g.

Test number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature (°C)	600	600	700	700	800	800	900	900
Fluidization agent	N_2	N_2/H_2O (70/30)	N_2	N_2/H_2O (70/30)	N_2	N_2/H_2O (70/30)	N_2	N_2/H_2O (70/30)

Once the reactor was at steady state, a batch of 5 g of fuel was injected down to the bed by two ball valves, falling through a stainless steel pipe ensuring that the DSS granulates reach the bed. The gas exiting the reactor passed through the cyclone and the tar sampling impinger train. The pipes connecting the reactor exit and the impinger train were heated to 330°C to prevent tar condensation. During the 60 to 120 s (depending on the temperature) that devolatilization lasts, 5 gas samples were taken with gas-tight syringes (see section 2.2.3.). Once the devolatilization is finished the remaining char was burned with air, the tar sampling train was washed and the gas samples analyzed.

As was mentioned in Chapter 2, the tests were conducted at a lower gas velocity than that in commercial FB units. However the test results are still applicable to commercial FB units: on the one hand, in the latter the operation is conducted at a gas velocity several times that of minimum fluidization but the heat transfer coefficient is hardly affected by the gas velocity because the fuel particles are converted in the emulsion where the flow conditions are close to that of minimum fluidization (the gas in excess pass in the form of bubbles). On the other hand, the mixing and uniform temperature in an industrial FB is achieved by using high gas velocity, since the bubbles are the stirring mechanism in the bed. In the present tests, the uniform temperature was achieved at the low gas velocities by keeping the fuel/bed material mass ratio low and by uniform distribution of the heat flux in the oven.

3. Results and discussion

This section presents the main results obtained during the tests concerning the light gas compounds, aromatic tars, gravimetric tars and their elemental composition. Different correlations found between light hydrocarbons and some tar compounds are also analyzed. Table 3.2 summarizes the experimental results presented in this chapter. Detailed composition of the aromatic tar is given in Appendix 2.

Table 3.2. Summary of results.

Test number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature (°C)	600	600	700	700	800	800	900	900
N_2 in the feeding (vol %)	100	70	100	70	100	70	100	70
Steam in the feeding (vol %)	0	30	0	30	0	30	0	30
Light gas analysis								
H_2 (mg/g fuel daf)	0.81	0.71	3.75	4.01	8.73	6.50	17.11	16.88
CO (mg/g fuel daf)	30.46	34.51	90.45	112.78	158.32	165.26	300.52	245.38
CO_2 (mg/g fuel daf)	92.44	168.86	140.80	220.07	205.32	281.50	232.77	357.29
CH_4 (mg/g fuel daf)	8.32	7.68	29.46	30.98	60.01	45.46	93.05	80.58
C_2H_4 (mg/g fuel daf)	7.64	8.54	41.88	41.75	37.05	50.98	69.64	60.02
C_2H_6 (mg/g fuel daf)	3.70	3.07	7.17	7.07	5.54	2.97	1.18	0.60
C_2H_2 (mg/g fuel daf)	0.10	0.10	0.61	0.93	2.41	1.73	5.87	5.06
C_3 (mg/g fuel daf)	8.17	5.60	22.73	19.33	9.92	6.58	0.89	0.45
GC-MS tar analysis								
Benzene (mg/g fuel daf)	4.45	4.31	25.76	20.37	50.40	50.94	77.39	76.06
Tar class 2 (mg/g fuel daf)	6.00	6.46	8.36	7.97	8.51	8.33	8.32	8.08
Tar class 3 (mg/g fuel daf)	14.45	12.77	28.27	27.82	28.04	27.00	16.31	12.88
Tar class 4 (mg/g fuel daf)	1.10	1.14	5.34	4.68	11.85	12.06	19.44	20.27
Tar class 5 (mg/g fuel daf)	0.20	0.20	0.37	0.33	1.05	0.92	2.14	1.93
Gravimetric analysis								
Gravimetric (mg/g fuel daf)	287	247	163	127	112	103	109	67
C in grav. (g/kg daf)	177	144	102	76	72	69	73	54
H in grav. (g/kg daf)	23	18	11	8	7	8	7	5
O in grav. (g/kg daf)	58	57	29	24	14	18	17	10
N in grav. (g/kg daf)	26	24	19	15	14	13	11	8
S in grav. (g/kg daf)	2	4	2	3	1	1	1	2

3.1. Light gas compounds

The yields of non-condensable gas species CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, and C3 (C_3H_8 and C_3H_6), at different reactor temperatures with and without steam are presented in Fig. 3.2. The trends obtained with the presence of steam are similar to those using only nitrogen, with some minor differences (analyzed below). In general, the trends are in agreement with previous works (Zhang et al., 2010; Xu & Tomita, 1989; Gomez-Barea

et al., 2010; Neves et al., 2011). The gas consists primarily of CO, CO_2 and the two main hydrocarbons CH_4 and C_2H_4. In absence of steam the total yield of gas increases from 152 g/kg DSS daf at 600°C to 721 g/kg DSS daf at 900°C. The yields of CO and H_2 increase with temperature, the latter showing a sharp increase from 800 to 900°C, due to the rapid enhancement of dehydrogenation of hydrocarbons and polymerization of tars; the maximum yield of H_2 measured in this work was 16.9 g/kg DSS daf at 900°C. The yield of CO_2 also increases with temperature but it seems to level off between 800 and 900°C. The yields of CH_4, C_2H_4 and C_2H_2 increase with temperature within the whole range of temperature investigated, reaching values of 93.0 and 69.6 g/kg DSS daf, respectively. The yield of C3 and C_2H_6 initially increases and sharply decreases at temperatures higher than 800°C, being insignificant compared with C_2H_2, C_2H_4 and CH_4 at 900°C. Maximum yields of C_3 and C_2H_6 were reached at around 700°C with measured values of 22.7 and 7.1 g/kg DSS daf, respectively. The initial increase in light saturated hydrocarbon species (ethane and C3) with temperature is explained by the dealkylation of substituted aromatic molecules (mechanism 3 in Fig. 3.1) and the breakage of long chain tars (Hayashi et al., 1992), both being present in the tars from DSS pyrolysis (Sanchez et al., 2009). The increase in the yields of unsaturated hydrocarbons such as ethylene or acetylene is due to dehydrogenation reactions of small saturated hydrocarbons and the fracture of primary tars at higher temperatures.

The main differences found between the tests with and without steam are the increase in the yield of (CO_2 + CO) and the CO_2/CO ratio. To explain these findings equations (1)-(3) include the most important steam reforming reactions taking place at high temperature.

$$\text{Light hydrocarbon } (C_XH_Y) + H_2O \rightarrow CO + H_2 + \text{tar } (C_\alpha H_\beta O_\gamma) \quad (1)$$

$$C_{CHAR} + H_2O \rightarrow CO + H_2 \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

The increase in the yield of (CO_2 + CO) is explained by the cracking and reforming of light hydrocarbons in reactions such as (1). At the higher range of temperature tested, i.e. between 800°C and 900°C, the contribution of char gasification (2) to the measured (CO_2 + CO) could also be significant, according to the rate of char gasification measured, in the order of 30%/min ($5 \cdot 10^{-3}$ s^{-1}) at 900°C (Nilsson et al., 2012). The increase in the CO_2/CO ratio with steam concentration can be explained by the enhancement of Reaction (3). According to Reactions (1-3) significant increase in hydrogen yields should have been measured in the presence of steam. However, this trend was not observed in the present work. The kinetic scheme of reactions is probably more complex than that indicated in Reactions 1-3; hydrogenation reactions could occur in parallel with those reactions, balancing the hydrogen concentration at high temperature in accordance to our measurements.

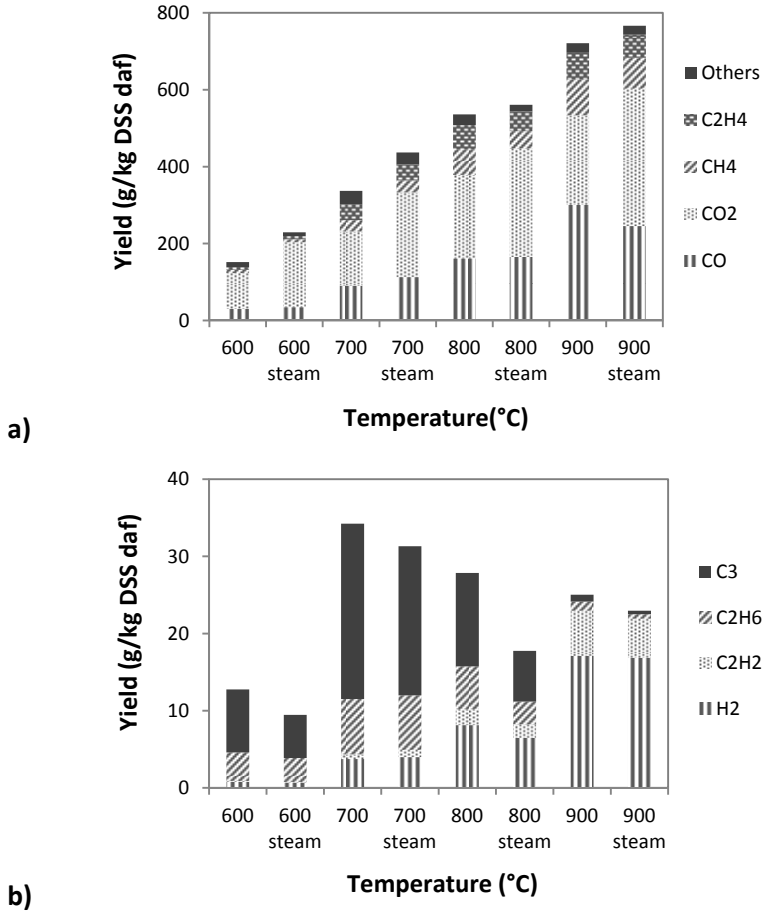


Fig. 3.2. Yields of gaseous species as a function of reactor temperature for tests with and without steam addition. 3.2a: yields of CO, CO_2, CH_4, C_2H_4 and others (sum of the yields of figure 3.2b compounds). 3.2b: yields of H_2, C_2H_2, C_2H_6 and C_3 (sum of C_3H_8 and C_3H_6).

3.2. Aromatic tar compounds

Fig. 3.3 presents the measured yields of aromatic tar compounds (grouped according to (van Paasen, 2004), see Table 2.2) as a function of temperature in tests with and without steam addition. The results reveal that steam has negligible influence on the aromatic tar yields, in agreement with published results (Zhang et al., 2010; Jess, 1996; Miura et al., 2003). At temperatures between 600°C and 750°C the yield of tar class 3 increases significantly, whereas it decreases at higher temperature. Tars with this behavior were classified by (Milne et al., 1998) as secondary tars (see Table 2.2).

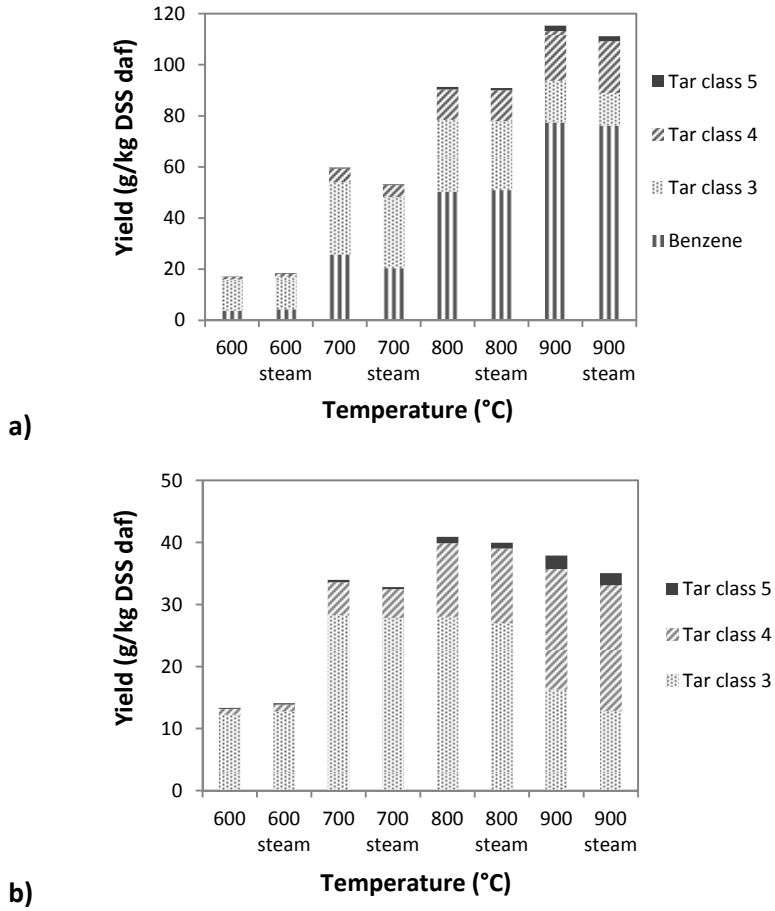


Fig. 3.3: Yields of aromatic tars as a function of reactor temperature for tests with and without steam addition. 3.3a: yields of benzene, tar class 3, tar class 4 and tar class 5. 3.3b: the same yields as Fig. 3.3a but free of benzene for a better visualization.

To understand the formation and subsequent conversion of aromatic tars during devolatilization the following analysis is made. The formation of tar class 3 proceeds through breakage and decarboxylation of primary tars (Cypres, 1987) and Diels-Alder reactions (involving small unsaturated hydrocarbons) followed by dehydrogenation (Morf et al., 2002; Ledesma et al., 2002a; Cypres, 1987). The subsequent thermal conversion of tar class 3 species above 750°C is explained by: (1) Direct combination of two aromatic species producing a dimer (Morf et al., 2002; Cypres, 1987; Bruinsma & Moulijn, 1988; Ledesma et al., 2000; Lu & Mulholland, 2004); (2) Addition of light unsaturated hydrocarbons to aromatic rings, like the HACA mechanism (hydrogen abstraction acetylene addition) related to PAH formation and growth (Morf et al., 2002; Ledesma et al., 2000; Thomas et al., 2007); and (3) dealkylation and dehydroxylation reactions (Jess, 1996; Ledesma et al., 2002a; Taralas et al., 2003). In fact, these mechanisms have influence on all aromatic species, not only on monoaromatic compounds (tar class 3). The two first mechanisms increase the

molecular weight of the tar mixture (see Fig. 3.1), producing heavy tars, while the third mechanism generates lower aromatic molecules such as benzene. Application of this analysis to the measurements obtained in this work makes it possible to conclude that benzene and light tars (tar class 2 and 3) are the main sources of heavy tars (tar class 4 and 5). Therefore the formation of heavy PAH is a sequential process (Ledesma et al., 2002a), i.e. heavy tars are formed once their precursors, i.e. light tars, have been produced.

The marked increase in the yield of acetylene at 900°C in Fig. 3.2b is most probably related with the increase in the yields of heavy tar observed at that temperature in fig. 3.3b. This is supported by the observations of Richter & Howard, 2000, in which unsaturated hydrocarbons such as acetylene have been identified to take key part in reactions leading to PAH growth and soot formation. In the present work the soot was not measured but an increase in soot yields at temperatures above 900°C has been measured in many works (Houben, 2004; Ledesma et al., 2002a; Li & Nelson, 1996; Williams & Taylor, 1993; Xu & Tomita, 1989), supporting the observations and conclusions made here.

Fig. 3.4 shows the effect of temperature on the yields of the main heteroatomic tar compounds; phenol, benzonitrile and thiophene. Once again steam seems to have little influence on tar yields. However the yield evolution of the three heteroatomic tars present significant differences when the temperature is increased. It is seen that benzonitrile and thiophene yields increase with temperature while the yield of phenol initially increases and then strongly decreases at temperatures over 700°C. This fact indicates that heteroatomic compounds with hydroxyl groups are more reactive than that with a cyano group or thiophene, in agreement with (Bruinsma et al., 1988).

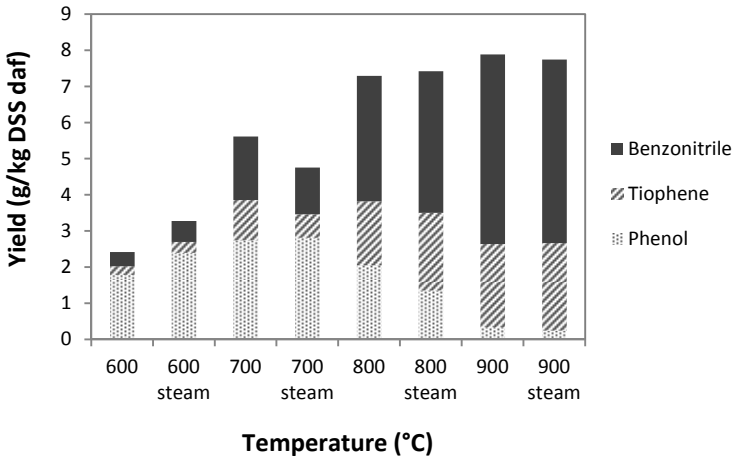


Fig. 3.4: Yields of the main heteroatomic tar compounds as a function of reactor temperature for tests with and without steam addition.

3.3. Gravimetric and elemental analyses

Fig. 3.5 compares the yields of tar compounds determined by gravimetric tar analysis to the so-called aromatic non-volatile tar (ANVT). The gravimetric tar mainly comprises the heavy heteroatomic compounds, non-aromatic tars and ANVT, since the BTX represent the bulk of light aromatic tars which are lost during vacuum distillation applied during determination of gravimetric tars. Therefore comparison of gravimetric tar with ANVT allows for establishment of the differences between the various tar compounds. This is made in Fig. 3.5, where the yields of gravimetric and aromatic tars (ANVT) are displayed as a function of temperature. It is shown that the gravimetric tar is nearly ten times higher than ANVT at 600°C, while it is only about two times that value at 900°C. It is observed that the gravimetric tar decreases significantly with temperature and slightly with steam concentration, whereas the ANVT (≈aromatic tars) increase with temperature and are not affected by steam. The difference found in the yields of the two types of tars at any temperature confirms that the tar compounds detected by GC-MS account for only a fraction of the total tar yield, even at 900°C. Since the GC-undetectable fraction could comprise high mass (or high polarity) tar compounds, the error made by estimation of the dew point of the mixture (Thersites) with only aromatic tars could be high.

Fig. 3.6 shows the results of the elemental analyses of the gravimetric tar and the elemental composition of ANVT, the latter calculated by taking into account the chemical structure of each single tar included in the ANVT. The oxygen yield was quantified by difference. However the gravimetric residue may contain also other elements such as Cl and AAEM that are not measured in the elemental analyses. Hence the real oxygen yield could be lower than that indicated in the figure.

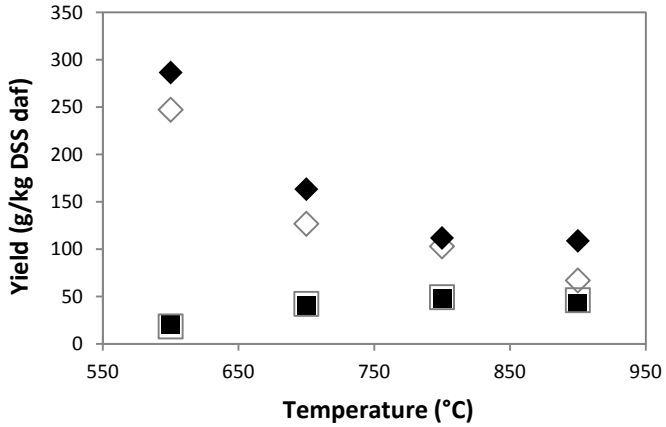


Fig. 3.5: Comparison between the yields of gravimetric tars and aromatic non-volatile tars (ANVT = GC tars – BTXs) compounds in tests with and without steam as a function of reactor temperature. ◆: gravimetric sample without steam addition. ◇: gravimetric sample with steam addition. ■: ANVT without steam addition. □: ANVT with steam addition.

In Fig. 3.6 the difference in the C-H-N-S-O yield between the two types of tars (gravimetric and ANVT) at a given temperature enables the estimation of the elemental composition of tar compounds that are not analyzed by GC-MS. The significant difference in oxygen found between the two tars displayed in Fig. 3.6, even at 900°C, questions the fact that oxygenated tars are fully converted at temperature higher than 800°C, as it is usually accepted (Zhang et al., 2010). The presence of salts in the gravimetric tar could partially explain this discrepancy. However an important portion of the carbon in the gravimetric sample was neither detected by GC-MS, indicating that even at temperatures over 800°C, the tar mixture contains a significant fraction of tars undetectable by GC-MS (mostly compounds with a high polarity).

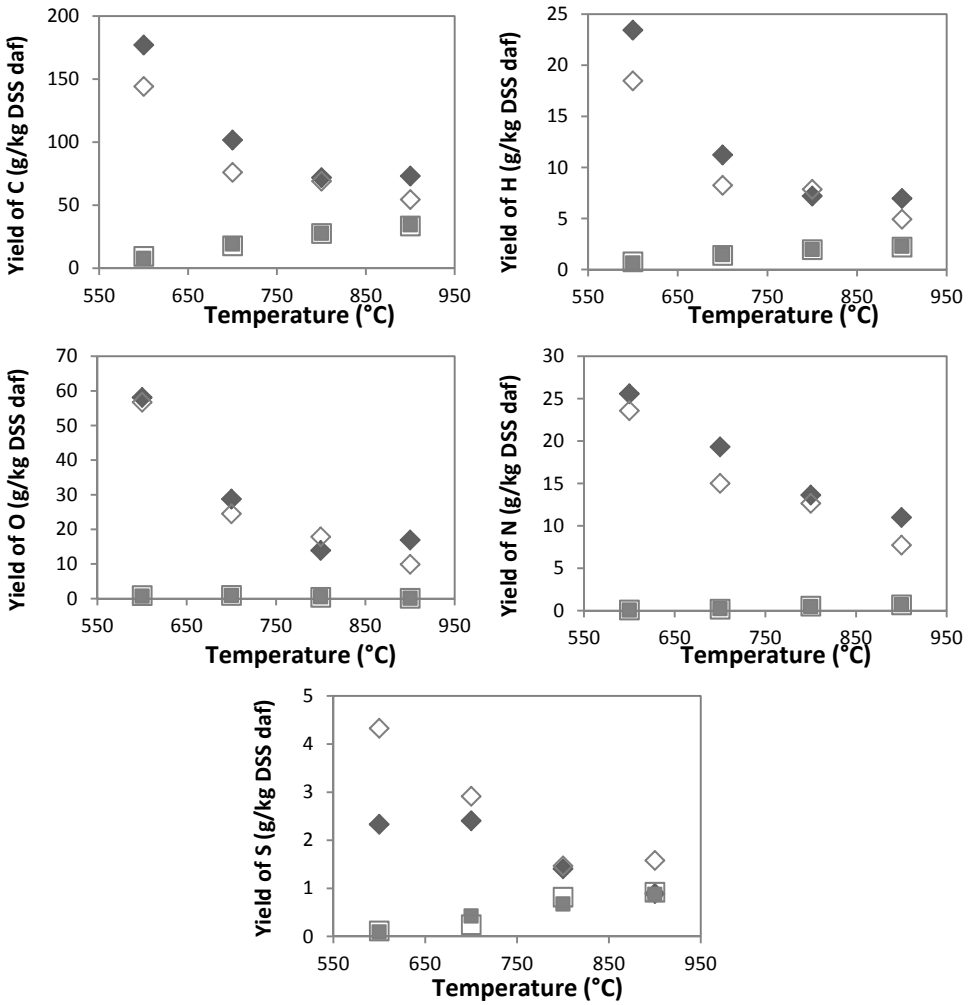


Fig. 3.6: Comparison between the yields of C, H, O, N and S in the gravimetric tar and in the tars analyzed by GC-MS (free of BTXs) as a function of reactor temperature. ◆: gravimetric sample without steam addition. ◇: gravimetric sample with steam addition. ■: ANVT without steam addition. □: ANVT with steam addition.

The high yield of nitrogen in the gravimetric residue (similar to that of oxygen at temperatures above 800°C) is due to the high nitrogen content in sewage sludge (van Paasen et al., 2006). The N fraction in the gravimetric residue is mostly undetectable by GC-MS (with the analytical method used here) and could be due to N-heteroatomic tars such those compounds found in (Chen et al., 2011) or to ammonium-salts such as ammonium chloride.

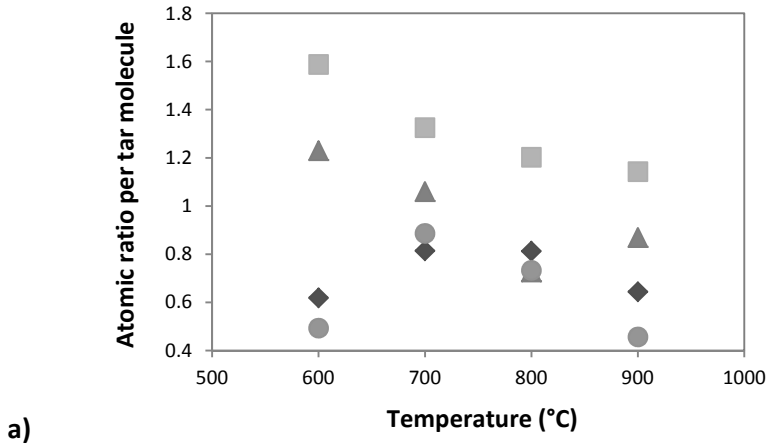
Sulfur in the gravimetric sample seems to be strongly influenced by the presence of steam in the lower range of temperature, i.e. 600°C-700°C. At 900°C the only molecule containing sulfur analyzed by GC-MS (thiophene) represents more than half of the total sulfur in the gravimetric residue. This fact suggests that at lower temperatures the sulfur-tars are mainly composed of alkyl-thiophenes, which are converted to thiophene at higher temperatures by dealkylation reactions.

Fig. 3.7 plots the atomic ratios of the gravimetric tar as a function of temperature with and without steam in the reacting gas. The representation allows estimation of a tar (with a formula $C_1H_xO_yN_zS_w$) resulting from devolatilization at different conditions. This is useful both for modeling tar conversion (Gómez-Barea & Leckner, 2010) (where an average tar compound after devolatilization at a given temperature has to be prescribed/assumed) and also for the closure of CHONS balances (Neves et al., 2011).

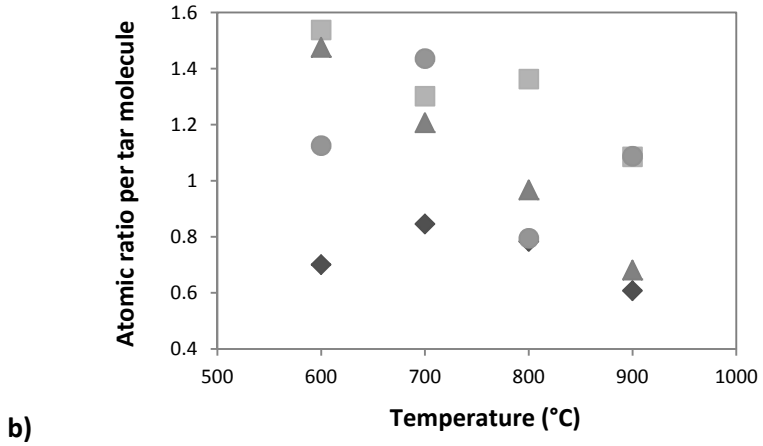
3.4. Interrelations between light gas and tar compounds

The light gas yields can be used as a shortcut method to estimate the main characteristics of the tar mixture (Dufour et al., 2011; Brage et al., 1996). Since the sampling and analysis of tars is an expensive and time-consuming process, the estimation of the main properties of the tar mixtures from light gas measurements enables to save considerable time, experimental effort and money.

As was previously commented light hydrocarbons and aromatic tars interact during the secondary conversion of volatiles. Both compounds (tars and hydrocarbons) are affected by the reactor conditions and suffer the same reactions such as dehydrogenation or C-C bond scission. The interaction of tars and light hydrocarbons during devolatilization depends on the fuel, reactor configuration, and operating conditions (mainly temperature and the presence of oxygen in the bulk gas mixture (Gómez-Barea & Leckner, 2010)). Hence, it is expected that some relations exist between tar composition and light hydrocarbons.



a)



b)

Fig. 3.7: Atomic ratios of H, O, N and S (normalized by that of C) in gravimetric tar in tests without steam addition (Fig. 3.7a) and with steam addition (Fig. 3.7b). ■: H/C (x). ▲: O/C x5 (y). ◆: N/C x5 (z). ●: S/C x100 (w), being x, y, z and w the subscripts in a generic gravimetric tar with formula: $C_1H_xO_yN_zS_w$

Fig. 3.8 presents the correlation between the yields of benzene and methane measured in the present work and that obtained by (Dufour et al., 2011) during pyrolysis of wood in a tubular reactor between 700°C and 1000°C. The difference in the values displayed was expected since very different biomass and experimental conditions were applied in the two works. Nevertheless, the correlations obtained in the two works present similar slopes, suggesting similar reaction pathways of methane and benzene formation. The lack of linear tendency at lower temperature can be explained by the scheme of benzene and methane formation in Fig. 3.9 (adapted from (Dufour et al., 2011)). Methane is formed by thermal decomposition of primary and secondary tars, whilst benzene is formed by the thermal decomposition of secondary tars (alkyl-aromatics) only. At 600°C decomposition of primary tars by de-alkylation reactions producing methane occurs to a significant extent, whereas the rate of

thermal conversion of secondary tars at 600°C is slow (Milne et al., 1998). Therefore the generation of benzene is enhanced at higher temperature only.

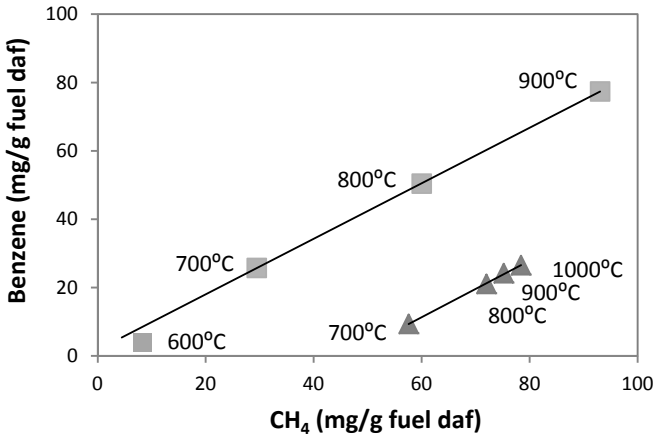


Fig. 3.8: Relation between the yields of benzene and methane (solid lines represent the fitting curves). ■: Results obtained in the present work at temperatures between 600°C and 900°C; the correlation follows the equation: $Y_{benzene}=0.812Y_{methane}+1.786$ (Y mg/g DSS daf). ▲: Results obtained by (Dufour et al., 2011) in the temperature range 700°C-1000°C.

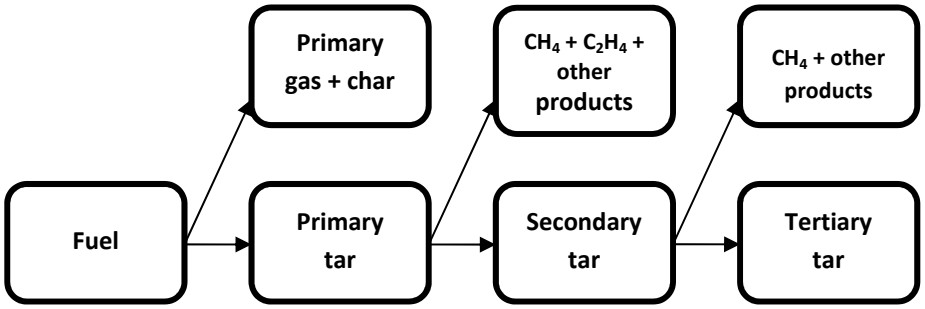


Fig. 3.9: Simplified scheme of methane, ethylene and tar formation (adapted from (Dufour et al., 2011)).

Similar sequential reactivity scheme could explain the relation measured between the yield of methane and the C/H ratio in the gravimetric residue, presented in Fig. 3.10. The correlation is seen to be linear between 700°C and 900°C, while the gravimetric residue becomes more aliphatic (lower C/H ratio) at 600°C. The C/H ratio for gravimetric tar is related with the degree of aromatization of tars (Hayashi et al., 1992), giving an indication of the main structural composition of the tar mixture. For example toluene and pyrene have C/H ratios of 10.5 and 19.2 respectively. Therefore,

the data of Fig. 3.10 indicate that gravimetric tars contain a significant proportion of aliphatic chains even at 900°C. This result was unexpected because the substituted aromatics are believed to be totally decomposed at temperatures above 700°C, giving CH_4 and the parent aromatic (Nelson et al., 1988). However it has been found in a recent publication (Namioka et al., 2009) that the gravimetric tar obtained during thermal cracking tests at 900°C and 4s of gas residence time contained a 15% of aliphatic hydrogen, indicating a significant presence of alkyl-aliphatic compounds even at this temperature.

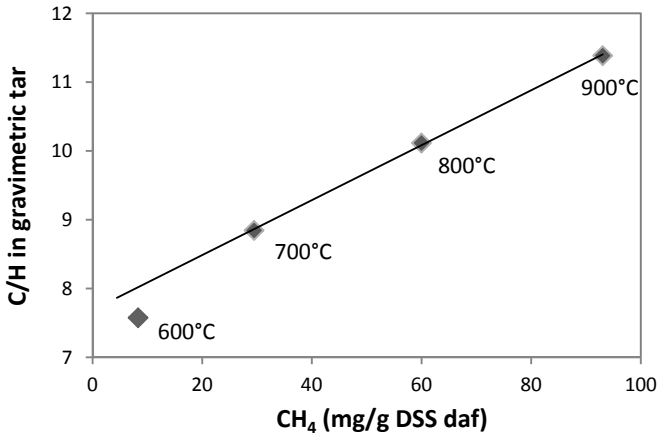
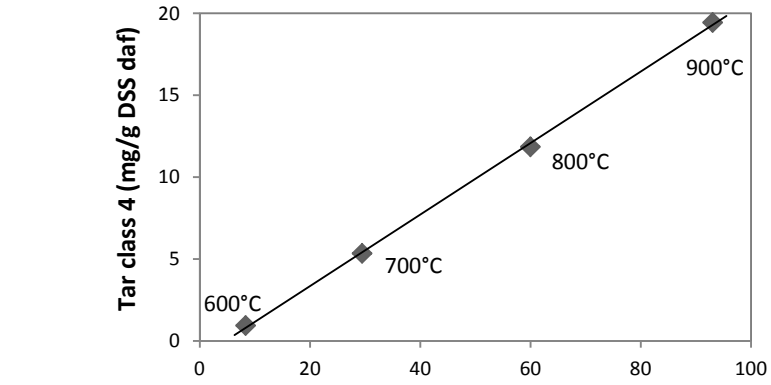


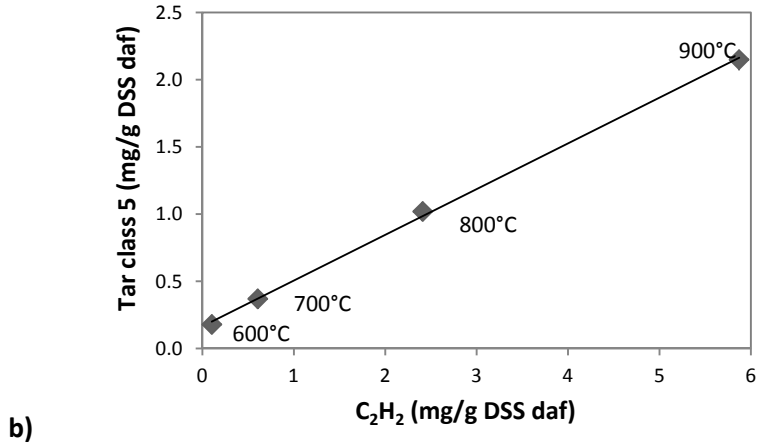
Fig. 3.10: C/H ratio in gravimetric tar as a function of methane yield at temperatures between 600°C and 900°C. The solid line was obtained by fitting the results for temperatures between 700°C and 900°C.

Fig. 3.11 shows the relations between methane and the yield of tar class 4 (Fig. 3.11a) and between acetylene and the yield of tar class 5 (Fig.3.11b). Both quantities are clearly correlated within the whole temperature range tested (600-900°C). The relation between the C_2H_2 and tar class 5 is especially interesting since it enables the estimation of the heavier tar class, which is the main responsible of the high tar dew point found in conventional FBG. Both compounds (C_2H_2 and tar class 5) are produced at high temperature from other species (C_2H_4 and tar class 4 respectively) and, in addition, the formation of tar class 5 (PAHs) is strongly related with the presence of acetylene in the reacting gas due to the HACA mechanism (tar class 5 is partly produced from the acetylene, see Mechanism 2 in Fig. 3.1).

Overall, the relations found indicate that, under the conditions tested, is possible to correlate the yields of certain light hydrocarbons with different tar properties or yields. However, these relations are expected to depend on the fuel used as shown in Fig. 3.8, and probably on other operation conditions. This makes it necessary to validate these correlations for other process conditions. The influence of the operating conditions on the relations between tars and hydrocarbons obtained here is further discussed in Chapter 4.



a)



b)

Fig. 3.11: Yields of tar class 4 and 5 as a function of the yields of methane and acetylene for tests without steam addition (solid lines represent the fitting curves). 3.11a: yields of tar class 4 vs methane yield at temperatures between 600°C and 900°C; the correlation follows the equation: $Y_{Tc4}=0.218Y_{methane}-1.016$ (being Y mg/g DSS daf). 3.11b: yield of tar class 5 vs acetylene yield at temperatures between 600°C and 900°C; the correlation follows the equation: $Y_{Tc5}=0.340Y_{acetylene}+0.165$ (being Y mg/g DSS daf).

4. Conclusions

In this chapter the effect of temperature (uniform along the reactor) and steam concentration on tar and light hydrocarbon production during devolatilization of dried sewage sludge (DSS) in a fluidized bed (FB) was investigated. The tests were conducted at temperatures between 600 and 900°C and steam concentrations of 0 (only nitrogen) and 30 vol%. This range of temperature includes the operation range of conventional (one-stage) FBG (800-900°C) but also lower temperatures that could be

attained in the first stage of the FLETGAS system. In Chapter 4 the work is extended to investigate the measures influencing the tar and light hydrocarbon composition in staged gasifiers where different temperature may exist in the bed and freeboard.

The main results obtained in this chapter are the following:

- Steam has negligible influence on the yields of aromatic tar (Fig. 3.3 and 3.4) and light hydrocarbon (Fig. 3.2) compounds. It has only a slight influence on the yield of gravimetric tar (aromatics + non-aromatics, see Fig. 3.5) demonstrating that steam only promotes decomposition of the non-aromatic fraction under the operating conditions tested.

- The results from the elemental analysis of gravimetric tars demonstrate that even at high temperature (900°C) the presence of heteroatomic (O, N and S) compounds is significant in the condensable fraction. The amounts of thiophene and benzonitrile measured by GC-MS confirmed the high stability of these compounds even at high temperatures. This finding is of relevance when using fuels with a high content in N or S, such as DSS, since the final tar composition could contain high proportion of these compounds. The oxygen found in the gravimetric tar, even at 900°C, questions the fact that oxygenated tars are fully converted at temperature higher than 800°C.

- The gravimetric tar, even at the highest temperature tested (900°C), doubled the yield of aromatic tars measured by GC-MS. This indicates that the tar mixture in the gas contains a significant fraction of undetectable (by GC-MS) tar compounds (Tar class 1, see Table 2.2). Since the GC-MS tars are commonly used to estimate the tar dew point, the high proportions of undetectable tars (that could be composed of heavy compounds condensing at high temperature) implies that these dew point estimations using the tar composition obtained by GC-MS is questionable, i.e. most probably the temperature at which the dew is formed will be higher than that calculated by standard procedure (dew point method from GC-MS analysis).

- The saturated hydrocarbons (C3 and C_2H_6) and alkyl-aromatic tars increased markedly when the temperature was raised from 600°C to 700°C, decreasing at higher temperature. The yields of CH_4, C_2H_2 and that of aromatic tars increased with temperature in the whole range of temperature studied (600-900°C).

- The interrelations between tar and light hydrocarbons composition enabled to correlate the yield of light hydrocarbons with various properties of the tar mixture (Fig. 3.8, 3.10 and 3.11), being a useful shortcut method for the estimation of the yield of heavy tars and aromaticity of the mixture. Besides, the analysis of the observed relations provides understanding of the mechanisms of tar conversion into light hydrocarbon species during devolatilization in an FB.

CHAPTER 4

Influence of the dense bed and freeboard temperature on the volatiles generated in a fluidized bed

The information obtained about FB fuel devolatilization in Chapter 3 is expanded in this chapter. The specific objective in this chapter is to study separately both the composition of the primary and secondary volatiles. Due to the fluid-dynamics and the properties of the fuel in a FBG, primary volatiles are mostly released from the particle in the dense bed, whereas the secondary volatiles are the result of the conversion of primary volatiles when they pass through the freeboard. Assuming these facts, in this chapter tests have been conducted in laboratory FB setting different temperatures in the two zones in an attempt to investigate their effects on the tar yields produced.

In particular, it was determined: 1- the influence the dense bed temperature and fuel particle size on the yield and composition of volatiles released from the fuel particles (with minimum secondary conversion), and 2- the role of freeboard temperature in the secondary conversion processes.

The tests were made by introducing a batch of dried sewage sludge (DSS) in a fluidized bed reactor fed by a continuous flow of nitrogen. Additional tests were conducted with wood pellets in order to compare the results of DSS with a typical biomass.

The final motivation of the investigation made in this chapter is to evaluate the improvements in the composition of gas (focused on tar reduction) that can be achieved by staging the gasification agent in autothermal FB gasifiers such as the FLETGAS.

1. Introduction

A fuel particle fed to a fluidized bed (FB) is dried and devolatilized, yielding char and volatiles. This is a thermally driven process occurring in the dense bed. After primary decomposition of volatiles within the particle, secondary conversion occurs in the reactor, where volatiles and char may be further cracked, oxidized or reformed in a series of complex homogeneous and heterogeneous reactions. A phenomenological, simplified, description of the processes occurring during fuel conversion in an FB fed by an inert fluidization agent (nitrogen) is illustrated in Fig. 4.1. The process has been divided into primary generation and secondary conversion of volatiles (Gómez-Barea & Leckner, 2010). In fact, the distinction made between primary and secondary processes, as well as between intra and extra-particle processes, is an approximate method to track the conversion of volatiles.

It is useful to distinguish two levels of description: the particle and the reactor levels. The reactor level includes mainly a dense bottom bed zone and a freeboard with a dilute flow of entrained fine solids. Once the volatiles are emitted from the particle (represented by "1" in Fig. 4.1) , they mix with the surrounding gas and are converted through secondary reactions resulting in secondary gas, char and tar, indicated by "2" in Fig. 4.1. Due to the fast release of volatiles, the gas surrounding the particle does not significantly penetrate into it during devolatilization and the rate and yield of species are quite insensitive to the composition of the surrounding gas. This is the reason why nitrogen is used in devolatilization tests even though the results are applied to gasification or combustion processes.

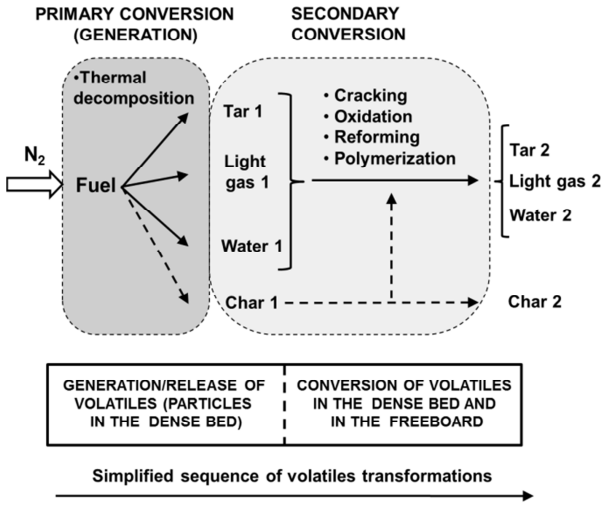


Fig. 4.1. Evolution of fuel, volatiles and char during fuel devolatilization in FB using nitrogen. Indication is made of the primary and secondary processes (subscripts "1" and "2") as well as the zones of the FB where these processes take place (the assumptions behind this simplified scheme are discussed in the main text).

The volatiles emitted from a particle meet the reactor atmosphere, whose temperature is higher than that inside the particle, because the heating up of the solid fuel occurs in parallel with the release of volatiles. This is the typical situation in FB where coarse, mm-sized, particles are employed. The volatiles react and change their chemical nature first during the way out from the particle and afterwards in the emulsion of the FB (outside of the particle). Primary tars comprise aliphatic and heteroatomic compounds, which are linked to the chemical structure of the parent fuel. These compounds are broken into lower hydrocarbon molecules and light gas, as well as into more stable aromatic structures by rearrangement of lower hydrocarbon chains. The extent of these changes depends on the rate of heating and temperature of the fuel during devolatilization, the temperature of the reactor (dense bed and freeboard), presence of catalysts and the residence time of volatiles within the particle and in the reactor. The temperature of a FB reactor (combustor or gasifier) mainly depends on the oxygen/fuel ratio of the operation. However, the heating rate and the temperature inside a particle depend on the fuel particle size and the rate of external heating (fluid-bed heat transfer). Fine fuel particles reach rapidly the bed temperature, devolatilizing without thermal gradients. In contrast, the devolatilization rate tends to be limited by the internal heat transfer in large particles, so these particles are devolatilized with temperature gradients. The effect of these factors on the yields of species emitted is qualitatively known for woody fuels, especially for small particles in the range of reactor temperatures between 500-700°C, i.e. focused on flash pyrolysis processes (Kersten et al., 2005). In contrast, less is known for coarse particles in FB operating between 700-900°C for non-woody fuels, i.e. focused on FB gasification of wastes (Petersen & Werther, 2005; Gómez-Barea et al., 2010).

Two types of experiments have been carried out to study these processes: (i) primary generation or formation tests, where the effects of conditions at which the particles are devolatilized in an FB are studied, trying to minimize the secondary reactions of the volatiles outside of the particles (Aguado et al., 2000; Stiles & Kandiyoti, 1989); and (ii) homogeneous secondary conversion tests, where the focus is on tracking the reactions occurring once the volatiles have been emitted from the particle (Morf et al., 2002; Sharma & Hajaligol, 2003; McGrath et al., 2001; Xu & Tomita, 1989; Hayashi et al., 1992; Hayashi et al., 1993; Ledesma et al., 2000; Williams & Taylor, 1993). Works addressing the tar formation in FB above 600°C minimizing the secondary conversion (Aguado et al., 2000; Stiles & Kandiyoti, 1989) have concluded that tar conversion is increased by rising the dense bed temperature. However neither of the two works (Aguado et al., 2000; Stiles & Kandiyoti, 1989) reported information about PAH formation. The homogeneous secondary thermal cracking of tars produced during the devolatilization of biomass (Morf et al., 2002; Sharma & Hajaligol, 2003; McGrath et al., 2001), coal (Nelson et al., 1988; Xu & Tomita, 1989; Hayashi et al., 1992; Hayashi et al. 1993; Ledesma et al., 2000) and wastes (Williams & Taylor, 1993) has been widely studied. Regardless of the fuel or the conditions at which primary volatiles were generated, these works have observed that overall (global or gravimetric) tar yield is reduced when the temperature is raised; dealkylation and fragmentation reactions are involved during tar conversion at these conditions, generating carbon monoxide, hydrogen, soot and PAH (Morf et al., 2002; Ledesma et al., 2000) as major products.

The effect of the particle size on the yields of the different products during FB devolatilization has been studied mainly for woody fuels and operation conditions applicable for flash pyrolysis technology (fine particles and temperature range of 400°C-700°C) (Kersten et al., 2005; Wang et al., 2005). Increasing the particle size diminished the tar yield during FB pyrolysis of sewage sludge at temperatures between 400°C and 700°C (Fonts et al., 2012). In contrast, when particle size of beech wood was modified from 800 μm to 6 mm an increase in tar yield was observed during pyrolysis at 800°C-950°C in a horizontal tube reactor (Chen et al., 2010). Higher PAH yield was measured by increasing particle size from 6 to 25 mm during FB pyrolysis of spherical wood particles in the temperature range of 500°C-900°C (Gaston et al., 2011). The increase in PAH compounds was attributed to the conversion of volatiles inside the particle.

In this chapter the formation and secondary conversion of volatiles during the devolatilization of DSS in a FB is studied. The focus is on detailed characterization of tars, with the purpose of shedding light on the mechanisms of reactions involved during thermal decomposition of tars at typical temperatures and gas residence times in autothermal staged FBG. To achieve these objectives the temperature of the dense bed and the freeboard were independently adjusted. This procedure enables to study the formation of volatiles at different bed temperatures reducing the secondary conversion by maintaining the freeboard temperature at 600°C as well as to study the secondary conversion of the volatiles generated at a given bed temperature for various freeboard temperatures. This way of operation expands the information acquired in Chapter 3, where the interest was to study the volatiles composition in a gasifier without thermal staging. Additionally, the influence of the particle size on DSS devolatilization products and the difference between wood and DSS volatiles are also investigated in this chapter.

2. Experimental procedure

The rig and the experimental procedure were similar to that described in Chapter 3. Fuel batches of 5 and 3 g were employed for tests using DSS and wood pellets respectively. Table 4.1 presents the operation conditions of the tests conducted in the present work. The tests conducted in absence of steam in the Chapter 3 are also included for comparison.

The tests have been divided in various sets, labeled according to the purpose of the tests (some tests are presented twice to facilitate the comparison of the tests carried out with a defined purpose).

- In the set of tests studying the generation of volatiles at different dense bed temperatures, tests 1-4, this temperature was varied between 500°C and 800°C, keeping the freeboard temperature at 600°C to minimize the secondary conversion of volatiles (Morf et al., 2002; Xu & Tomita, 1989; van Paasen, 2004); therefore the results from these tests are expected to represent the volatiles emitted from the particle (generation tests).

Table 4.1. Summary of tests conducted.

	Primary generation of volatiles				Secondary conversion of volatiles			Tests with uniform temperature along the reactor (+)				Influence of the particle size			Wood tests		
Test number	**1**	**2**	**3**	**4**	**1**	**5**	**6**	**2**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Fuel	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	Wood	Wood	Wood
Range of particle size (mm)	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	1-1.4	2-2.8	4-5	6^{X}	6^{X}	6^{X}
Dense bed temperature* (°C)	500	600	700	800	500	500	500	600	700	800	900	800	800	800	500	800	500
Freeboard temperature* (°C)	600	600	600	600	600	700	800	600	700	800	900	800	800	800	600	600	800

*: Set point

X: diameter of the pellet

+: The same temperature at both dense bed and freeboard

- In the set of tests 1, 5-6, the secondary conversion of the volatiles generated at the lowest dense bed temperature, i.e. 500°C, was investigated by modifying the freeboard temperature from 600°C to 800°C.
- The tests 2 and 7-9 were conducted by setting the same temperature both in the dense bed and freeboard, varying it from 600°C to 900°C (these tests belong to Chapter 3).
- The tests to study the particle size, tests 10-12, were conducted keeping the temperature of both dense bed and freeboard at 800°C.
- Additional tests (13-15) were carried out using wood pellets, applying the extreme values of temperature of dense bed and freeboard used for the DSS tests.

Two or three tests were conducted for each operation condition, showing high repeatability.

Due to the low gas velocity used in the tests (almost two times that of minimum fluidization), the bed material (dense bed) is slightly expanded and the number and size of bubbles are limited. As a result it was expected that mixing of fuel particles during their devolatilization in the dense bed was not significant. Visual observations made in dedicated experiments (Nilsson, 2012) suggested that the fuel particle remains most of devolatilization time (first 30-60 s) in the upper part of the bed, close to the bed surface. As a result, conversion of volatiles in the dense bed of the reactor is expected to be limited and secondary conversion of volatiles will take place mainly in the dilute zone (upper part of the bottom zone, transition zone and freeboard, see Fig. 2.3). This fact enables to study (tests 1-4) the volatiles formation in fluidized bed minimizing its conversion within the dense bed. This situation is common in commercial fluidized bed units since the inherent floatability of fuel particles during devolatilization maintains the fuel particles close to the upper zone of the dense bed.

2.1. Control of temperatures in bed and freeboard

Figure 4.2 presents the temperature measured along the reactor (points) and the set points (dashed lines) in the two zones for tests with extreme temperature differences between both zones (tests 4 and 6). The adjustment of temperature in the dense bed and in the upper part of the freeboard was quite good since the measured temperatures are seen to be close to the set points. Although only one measurement of the dense bed temperature is plotted in the figure (that used for the temperature control), this zone was checked to be at uniform temperature (by additional thermocouples inserted in dedicated tests). In contrast, considerable deviation is found in the intermediate zone. Ideally, the transition of temperature from the dense zone to the freeboard should be more abrupt than that measured. Nevertheless, the tests presented in Fig. 4.2 are the most unfavorable scenarios tested in the present work, i.e. with the highest temperature difference between the two zones. Therefore, it is considered that the temperature profiles achieved were good enough for the present investigation.

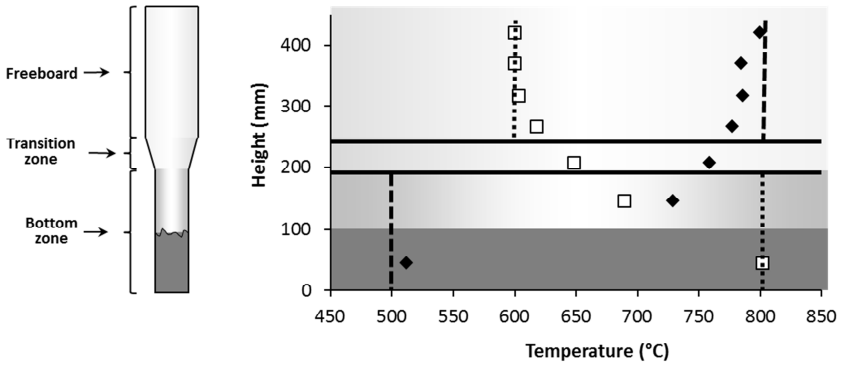


Fig. 4.2. Temperature profiles of Tests 4: □ and 6: ◆ (see Table 4.1).

3. Results and discussion

The detailed results for all tests conducted in this work are presented in Table 4.2. The data in the table include the main process conditions of the tests (grouped and numbered according to the purpose of the tests as in Table 4.1), the yields of light gas and the yields of tar compounds grouped as explained above (see Section 1.4). The detailed analyses of the influence of the different parameters studied are discussed in the following sections.

3.1. Formation of volatiles at various dense bed temperatures

Fig. 4.3a and 4.3b show the light gas yields measured at different dense bed temperatures at a fixed freeboard temperature of 600°C (Tests 1-4 in Table 4.1). As seen the yields of all the gas species increase with temperature. The yields of CO_2 and H_2 are in agreement with those measured for DSS pyrolysis tests in FB (Piskorz et al., 1986). Since CO is the most important product of homogeneous tar conversion (Morf et al., 2002), the low CO yield obtained here compared with that presented in (Piskorz et al., 1986), indicates that tar conversion is lower in the present tests. The yields of light hydrocarbons (Fig. 4.3b) increased with the dense bed temperature, although different behavior is found for the various hydrocarbons analyzed. C_2H_4 and CH_4 are the most abundant hydrocarbons measured, showing a constant increase within the entire range of temperature analyzed. In contrast, the yields of C_2H_6 and C_3 leveled off between 700°C and 800°C, indicating the initial decomposition of these compounds.

Table 4.2. Summary of tests conducted and yields of light gas and tar obtained.

	Primary generation of volatiles				Secondary conversion of volatiles			Tests with uniform temperature along the reactor (+)				Influence of the particle size			Wood tests		
Test number	**1**	**2**	**3**	**4**	**1**	**5**	**6**	**2**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Fuel	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	DSS	Wood	Wood	Wood
Range of particle size (mm)	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	2-2.8	1-1.4	2-2.8	4-5	6^X	6^X	6^X
Dense bed temperature* (°C)	500	600	700	800	500	500	500	600	700	800	900	800	800	800	500	800	500
Freeboard temperature* (°C)	600	600	600	600	600	700	800	600	700	800	900	800	800	800	600	600	800
H_2 (mg/g fuel daf)	0.57	0.81	2.60	4.06	0.57	2.64	5.99	0.81	3.75	8.73	17.11	-	-	-	-	-	-
CO(mg/g fuel daf)	26.72	30.46	52.96	66.58	26.72	70.36	114.14	30.46	90.45	158.32	300.52	-	-	-	-	-	-
CO_2 (mg/g fuel daf)	101.53	92.44	126.36	170.73	101.53	176.93	174.57	92.44	140.80	205.32	232.77	-	-	-	-	-	-
CH_4(mg/g fuel daf)	5.66	8.32	14.26	19.73	5.66	22.86	36.12	8.32	29. 46	60.01	93.05	-	-	-	-	-	-
C_2H_4(mg/g fuel daf)	6.96	7.64	12.78	20.48	6.96	42.41	41.44	7.64	41.88	37.05	69.64	-	-	-	-	-	-
C_2H_6 (mg/g fuel daf)	2.44	3.70	5.04	4.93	2.44	8.10	3.72	3.70	7.17	5.54	1.18	-	-	-	-	-	-
C_2H_2(mg/g fuel daf)	0.11	0.10	0.13	0.27	0.11	0.37	2.31	0.10	0.61	2.41	5.87	-	-	-	-	-	-
C_3(mg/g fuel daf)	5.54	8.17	12.79	13.30	5.54	15.48	12.21	8.17	22.73	9.92	0.89	-	-	-	-	-	-
Total light hydrocarbon (mg/g fuel daf)	20.71	27.93	45.00	58.71	20.71	89.22	95.80	27.93	72.39	114.93	170.63	-	-	-	-	-	-
Benzene(mg/g fuel daf)	3.02	4.45	5.60	13.51	3.02	11.05	55.10	4.45	25.76	50.40	77.39	31.78	34.34	33.08	1.59	15.53	30.63
Tar class 2(mg/g fuel daf)	6.54	6.00	7.72	8.38	6.54	7.41	8.17	6.00	8.36	8.51	8.32	7.40	8.00	7.46	3.83	9.54	6.78
Tar class 3(mg/g fuel daf)	14.27	14.45	18.13	22.17	14.27	24.56	34.11	14.45	28.27	28.04	16.31	26.66	28.80	26.97	2.53	13.01	16.96
Tar class 4(mg/g fuel daf)	1.22	1.10	2.29	3.20	1.22	4.08	8.79	1.10	5.34	11.85	19.44	12.15	12.21	12.81	0.76	3.37	6.21
Tar class 5(mg/g fuel daf)	0.20	0.20	0.17	0.25	0.20	0.44	0.88	0.20	0.37	1.05	2.14	1.20	1.18	1.33	0.19	0.24	0.40
Total GC-MS (mg/g fuel daf)	25.25	26.20	33.91	47.51	25.25	47.54	107.05	26.20	68.10	99.85	123.60	79.19	84.53	81.65	8.90	41.69	60.98
Gravimetric (mg/g fuel daf)	335	287	299	211	335	211	122	287	163	112	109	133	112	119	218	122	82

*: Set point

-: Measurement no available

X: Diameter of the pellet

+: The same temperature at both dense bed and freeboard

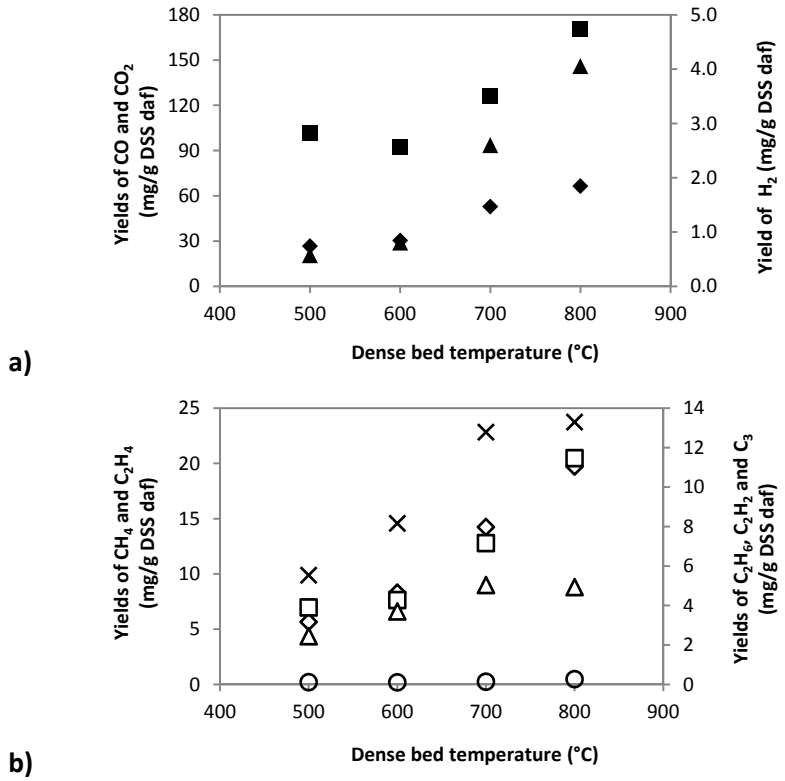


Fig. 4.3. Yields of light gases as a function of the dense bed temperature obtained during primary generation tests (Tests 1-4, see Table 4.1) with freeboard temperature of 600°C. 4.3a: yields of CO (◆), CO_2 (■) and H_2 (▲). 4.3b: yields of CH_4 (◇), C_2H_4 (□), C_2H_6 (△), C_2H_2 (○) and C_3 (×, sum of C_3H_8 and C_3H_6).

The gravimetric tar analysis is presented in Fig. 4.4a. It is seen that it is only slightly affected by the dense bed temperature between 500°C and 700°C, indicating a low extent of secondary conversion reactions. These results contrast with those presented in literature (Aguado et al., 2000; Stiles & Kandiyoti, 1989), where a strong decrease of tar yields was measured for the same range of temperature. The apparent disagreement could be explained by the short residence time of volatiles in the dense bed in the present work compared to that used in (Aguado et al., 2000) and (Stiles & Kandiyoti, 1989). As explained in Section 4.2, in the present study the fuel particles kept floating near the bed surface during devolatilization. As a result, the time of exposure to the dense bed conditions was limited and so was the extent of secondary conversion of volatiles in the dense bed. In Fig. 4.4a it is seen that the gravimetric tar yield was reduced by 30% when the dense bed temperature was increased from 700°C to 800°C, indicating that a bed temperature of 800°C is high enough to decompose significantly primary tars, even at short residence time.

In Fig. 4.4b the aromatic tar grouped in classes (see table 2.2) are presented. The small increase with temperature observed for the heavy aromatic tar compounds is remarkable. The only aromatic compounds that increase significantly with the dense bed temperature are those with low molecular weight, mostly benzene and naphthalenes (included in Tar class 4). Although it cannot be seen in Fig. 4.4b, naphthalene and methyl-naphtalenes, i.e. the lightest compounds of the class 4, comprise most of the yield measure of Tar class 4; Tar class 5, i.e. heavy PAH, is almost insensitive to the increase in the dense bed temperature within the range investigated. These observations are in agreement with previous results (Ledesma et al., 2002), indicating that formation and growth of aromatic tars is a sequential process of polymerization reactions. PAH is known to be the product of secondary reactions at high temperature involving tar compounds with low molecular mass and light hydrocarbons. Therefore low residence time of volatiles at the devolatilization temperature (dense bed temperature in our tests) is not enough to enhance the reactions leading to heavy PAH. It is concluded that high temperature and low gas residence time promote the reduction of gravimetric tar yield, but the formation of heavy PAH is limited.

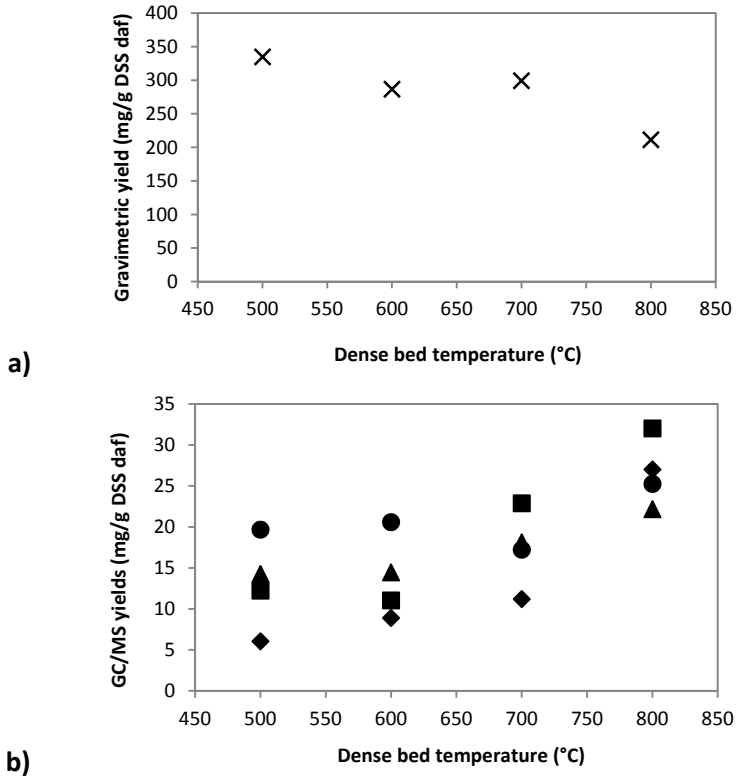


Fig. 4.4. Yields of tars as a function of the dense bed temperature for generation tests (Tests 1-4, Table 2) with freeboard temperature of 600°C. 4.4a: yield of gravimetric tar. 4.4b: Yields of benzene x2 (◆), Tar class 3 (▲), Tar class 4 x10 (■) and Tar class 5 x100 (●).

In order to assess the effect of particle size of DSS on the tar yields discussed above, various tests were conducted varying the particle size from 1-1.4 mm to 4-5 mm (see Table 4.1). The effect of particle size on the yields of tars is shown in Fig. 4.5. It is seen that the yields of aromatic and gravimetric tars are not significantly influenced by the particle size. These observations contrast with results from (Gaston et al., 2011), who found an increase in higher aromatic tars when using coarser wood spheres in the diameter range of 6-25 mm.

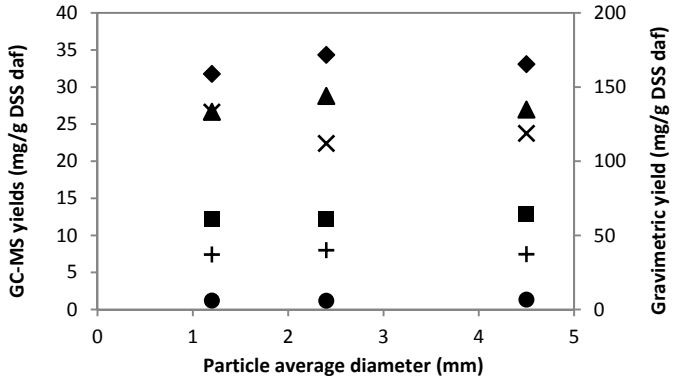


Fig. 4.5. Yields of tars as a function of the particle size: Yields of gravimetric tar (✕), benzene (◆), Tar class 2 (+), Tar class 3 (▲), Tar class 4 (■) and Tar class 5 (●).

3.2. Secondary conversion of volatiles

The secondary thermal treatment of the volatiles produced at a dense bed temperature of 500°C is studied for various freeboard temperatures in Fig. 4.6 and 4.7. Fig. 4.6 presents the yields of the different light gases with freeboard temperatures of 600°C, 700°C and 800°C. The increase in the gas yields is related with the thermal decomposition of primary tars generated during fuel devolatilization in the dense bed. The increase in the yield of CO_2 with temperature up to 700°C is related to the decomposition of carboxylic acids (Nelson et al., 1988), which accounts for the major part of tar species released during pyrolysis of DSS at low temperature (Sanchez et al., 2009), disappearing when the temperature is increased above 700°C (Evans & Milne, 1987). The yield of CO_2 between 700°C and 800°C is roughly constant, indicating that CO_2 is not a major product of secondary (or aromatic) tar decomposition, in agreement with observations made for coal (Nelson et al., 1988). The continuous increase in the yields of CO and H_2 observed in Fig. 4.6a are in agreement with previous work using wood (Morf et al., 2002), where the increase of these compounds is justified by the tar decomposition reactions at temperatures above 680°C. The CO is mainly produced during thermal decomposition of O-heteroatomic compounds, whereas H_2 is produced during dehydrogenation and polymerization reactions.

The variations of the yields of light hydrocarbons with temperature presented in Fig. 4.6b follow the same trend reported in (Xu & Tomita, 1989). The yields of C_2H_6 and C_3 species initially increase with temperature due to the breakage of longer aliphatic

chains but decrease when the temperature is raised above 700°C due to dehydrogenation and C-C bond scission reactions. However the yields of unsaturated hydrocarbons increase with temperature within the whole temperature range studied.

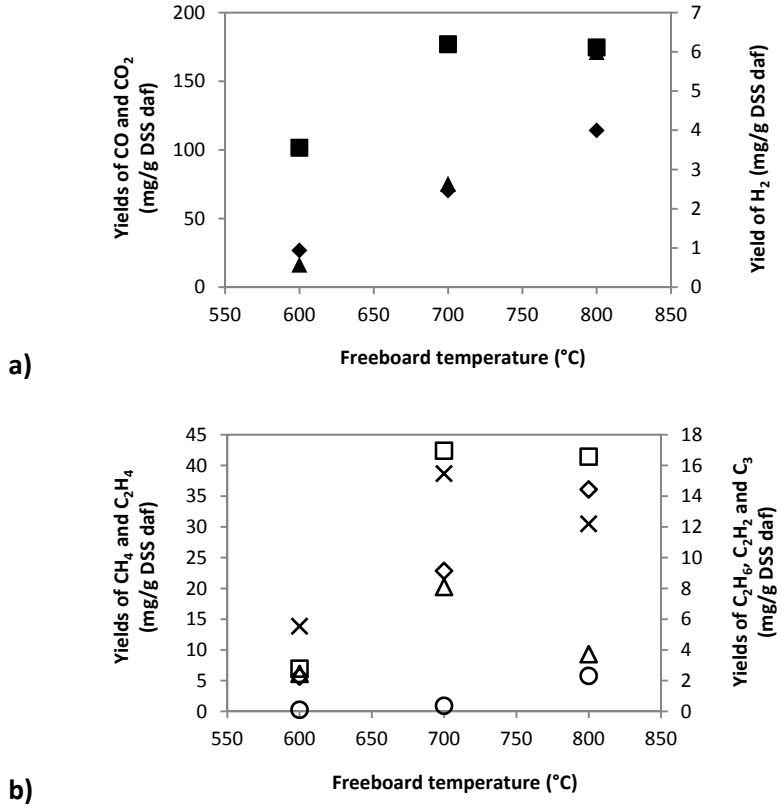


Figure 4.6. Yields of light gases as a function of the freeboard temperature for secondary tests (Tests 1,5-6, Table 4.1) with dense bed temperature of 500°C. 4.6a: Yields of CO (◆), CO_2 (■) and H_2 (▲). 4.6b: Yields of CH_4 (◇), C_2H_4 (□), C_2H_6 (△), C_2H_2 (○) and C_3 (×, sum of C_3H_8 and C_3H_6).

Fig 4.7 presents the yield of total light hydrocarbons (TLH) for generation and secondary conversion tests. The yield of TLH increases with the temperature of both the freeboard and the dense bed, however the increase in TLH yield is significantly higher when increasing the former. When increasing the dense bed temperature at fixed freeboard temperature (diamond marker in Fig 4.4), the net increase in the yield of TLH was significantly lower (from 20.7 to 58.7 mg/g DSS daf) than that found varying the freeboard temperature at fixed dense bed temperature (square marker in Fig. 4.4), which increased from 20.7 to 95.8 mg/g DSS daf. Taking into account these results, it is concluded that the secondary degradation of the primary tars in the freeboard is the main source of light hydrocarbons rather than their formation within the particle in the dense bed. This result is supported below by the analysis made for different tar compounds.

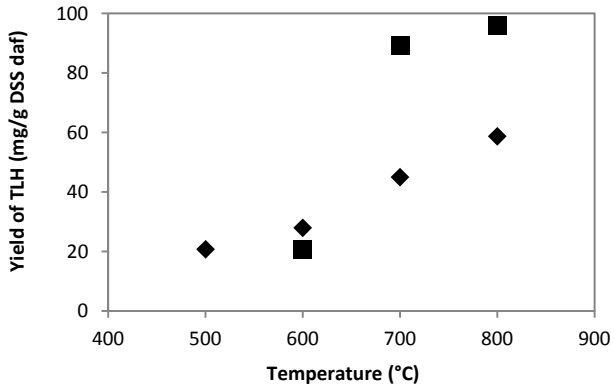
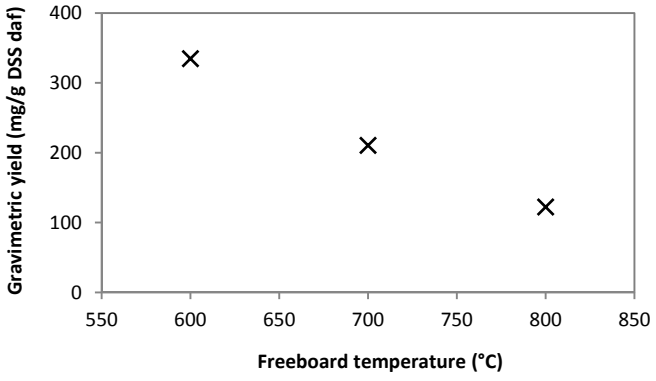


Fig. 4.7. Yields of total light hydrocarbons (TLH) for tests varying the dense bed temperature at fixed freeboard temperature of 600°C (tests 1-4, ◆) and for tests varying the freeboard temperature at fixed bed temperature of 500°C (tests 1,5-6, ■).

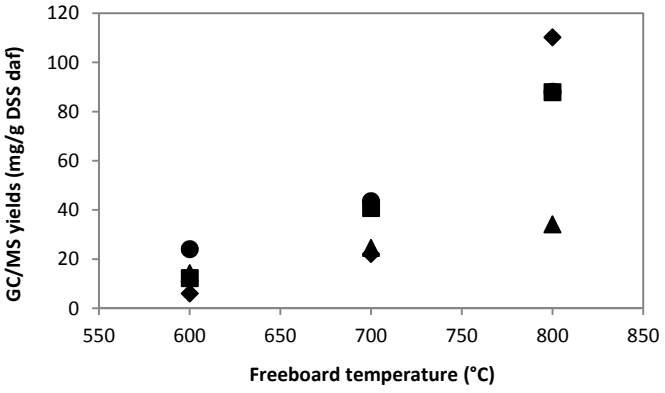
The evolution of the gravimetric tar yield is shown in Fig. 4.8a. As expected, the gravimetric tar yield is strongly influenced by the secondary thermal treatment. The decrease in the yield of gravimetric tar, from 335 g/Kg DSS daf at 600°C to 122 g/Kg DSS daf at 800°C, is in agreement with that presented by (Morf et al., 2002); the agreement is remarkable since very different fuels and reactor devices are used in the two works. Fig. 4.8b presents the variation of aromatic tars with temperature, showing that the rise of the freeboard temperature is accompanied by a strong increase in the yield of heavy aromatic tars (Tar class 4, Tar class 5) and benzene, while the yields of Tar class 3 only increases slightly. These results highlight that the exposure to temperatures above 700°C for gas residence time of 1 second enhances the formation of PAH.

Fig. 4.9a, 4.9b and 4.9c present the yields of aromatic tars and light gas from two tests at different configurations: 1- test with dense bed temperature of 500°C and freeboard temperature of 800°C (Test 6) and 2- test with both zones at the same temperature of 800°C (Test 8). The increase in the dense bed temperature reduces the yield of Tar class 3 but enhances the formation of Tar class 4 and 5. Nevertheless, the similar values of the yield of aromatics obtained in the two tests indicate that the presence of aromatic compounds in the final gas is mainly influenced by the temperature in the freeboard (by the homogeneous thermal treatment) rather than the dense bed temperature. This result is consistent with the small volatile conversion in the dense bed obtained during primary (generation) tests. The yields of gravimetric tar are also similar in both conditions, 122 g/Kg DSS daf in the tests with thermal stratifications (Test 6) and 112 g/Kg DSS daf in the tests with the whole reactor at 800°C (Test 8). The yields of light gas compared in Fig. 4.9b and 4.9c show that the carbon oxides and hydrogen are significantly affected by the dense bed temperature. Light hydrocarbons are comparatively less affected by the dense bed temperature with the exception of methane, whose yield is doubled when rising the dense bed temperature from 500°C to 800°C. From these results it can be concluded that the temperature at which

devolatilization occurs (that of the dense bed in the present work assuming that DSS particles reach the bed temperature rapidly) has a minor effect on tar and light hydrocarbon yields, while it enhances the production of CO, CO_2 and H_2 when it is increased from 500°C to 800°C.



a)



b)

Figure 4.8. Yields of tars as a function of the freeboard temperature for secondary conversion tests (Tests 1, 5-6, Table 4.1) with dense bed temperature of 500°C. 4.7a: yield of gravimetric tar. 4.7b: yields of benzene x2 (◆), Tar class 3 (▲), Tar class 4 x 10 (■) and Tar class 5 x100 (●).

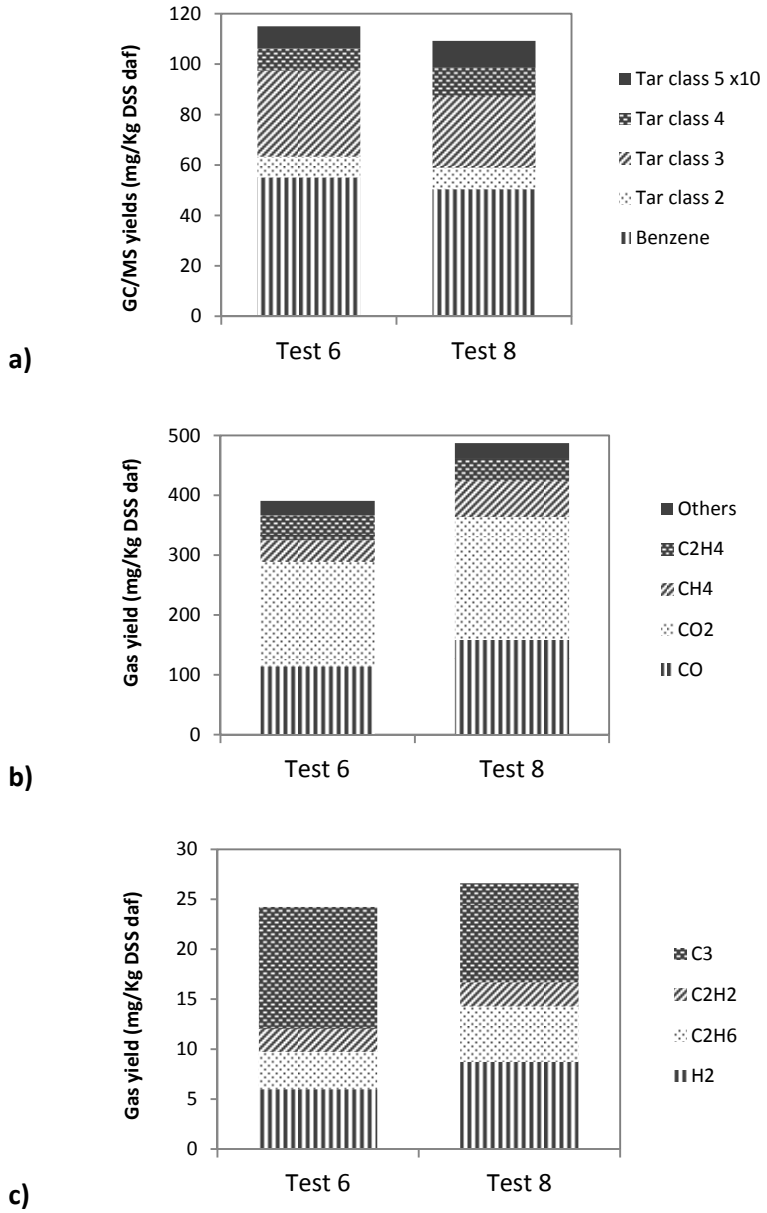


Figure 4.9. Comparison of yields of aromatic tar obtained in Tests 6 (dense bed temperature of 500°C and freeboard temperature of 800°C) and 8 (dense bed temperature of 800°C and freeboard temperature of 800°C): Yields of tars (4.8a) and light gases (4.8b and 4.8c).

3.3. Comparison between DSS and wood devolatilization products

In order to establish the differences in the nature of tars produced during devolatilization of DSS and wood, the results of several tests conducted with DSS and wood in similar conditions are shown in Table 4.3. It is seen that the yields of the different tar classes depend on the fuel. However, the same conversion trends for tars with temperature are obtained for the two fuels. This suggests that the same conversion mechanisms are involved in the tar maturation (secondary conversion) regardless of the parent fuel. Tar class 3 and gravimetric tar yields are clearly lower for wood than for DSS, however the differences observed in PAH yields (Tar classes 4 and 5) are small. Two main findings are underlined from the observations made (i) the yield of gravimetric tar and monoaromatic tar compounds are strongly linked to the parent fuel structure, being higher for DSS than for wood and (ii) the yield of PAH is mainly determined by the temperature in the reactor, being practically independent of the parent fuel structure. Since the tar dew point of the gas from an FB gasifier is determined to a great extent by the heaviest tars produced in the process, it can be concluded that the gas produced during DSS gasification and wood gasification is expected to have similar tar dew point (assuming that no drastic primary measures are applied in the reactor, which could significantly change the pyrolytic nature of the produced gas (Gómez-Barea & Leckner, 2009; Gómez-Barea & Leckner, 2010)).

Table 4.3. Comparison of tar yields for tests conducted with DSS (particle size: 2-2.8 mm) and wood (particle size: 6 ^{X} mm).

	DSS tests			Wood tests		
Test number	**1**	**4**	**6**	**13**	**14**	**15**
Dense bed temperature* (°C)	500	800	500	500	800	500
Freeboard temperature* (°C)	600	600	800	600	600	800
Benzene (mg/g fuel daf)	3.02	13.51	55.10	1.59	15.53	30.63
Tar class 2 (mg/g fuel daf)	6.54	8.38	8.17	3.83	9.54	6.78
Tar class 3 (mg/g fuel daf)	14.27	22.17	34.11	2.53	13.01	16.96
Tar class 4 (mg/g fuel daf)	1.22	3.20	8.79	0.76	3.37	6.21
Tar class 5 (mg/g fuel daf)	0.20	0.25	0.88	0.19	0.24	0.40
Total GC-MS (mg/g fuel daf)	25.25	47.51	107.05	8.90	41.69	60.98
Gravimetric (mg/g fuel daf)	335	211	122	218	122	82

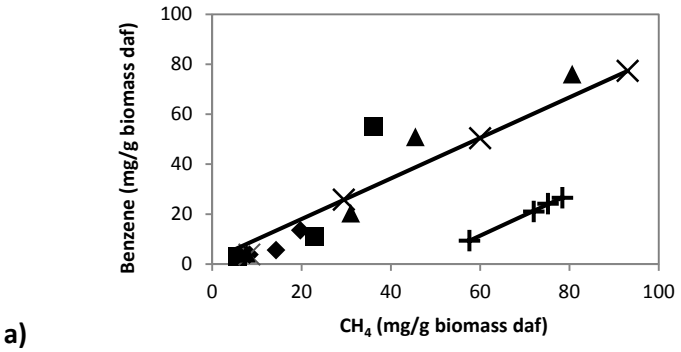
*: Set point

X: diameter of the pellet

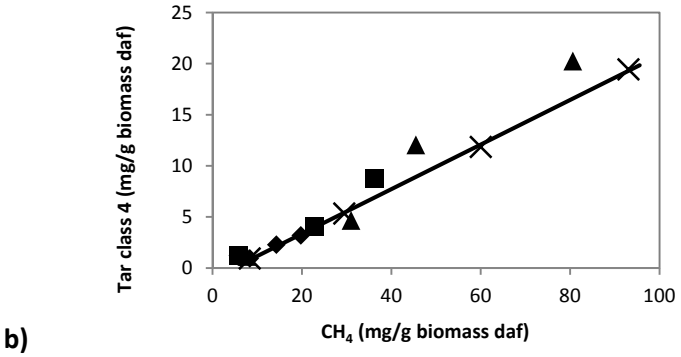
3.4. Interrelations between light gas and tar; validation

In Chapter 3 some interrelations between different light hydrocarbon yields and the yields of different tar classes were obtained. These interrelations comprise cross-functions of methane-benzene, methane-Tar class 4 and acetylene-Tar class 5. These correlations were obtained with uniform temperature along the FB reactor and in absence of steam. It was found that the interrelations were significantly influenced by the fuel used and some of them were only valid in a limited range of temperature as indicated Fig. 3.8 and 3.10. Below, the validity of the correlations obtained in Chapter

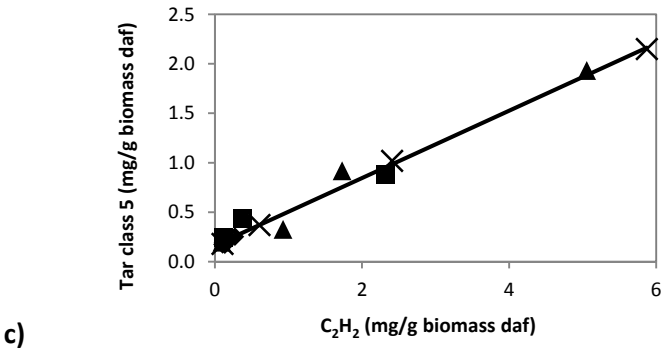
3 in conditions of thermal stratification of the reactor and in the presence of steam (for the latter the data are taken from Chapter 3) is studied.



a)



b)



c)

Fig. 4.10: Yields of benzene, tar class 4 and 5 as a function of the yields of methane, methane and acetylene for different operating conditions. Solid lines represent the fitting curves for tests with homogeneous temperature and without steam addition (**x** markers). 4.10a: yields of benzene vs methane yield. 4.10b: yields of tar class 4 vs methane yield. 4.10c: yield of tar class 5 vs acetylene. ▲ : steam addition tests. ◆: generation tests. ■: secondary conversion tests. **+**: results for wood obtained by (Dufour et al., 2011).

Figures 4.10a, 4.10b and 4.10c present the CH_4-benzene, CH_4-Tar class 4 and C_2H_2-Tar class 5 interrelations. The cross markers belong to the data obtained in tests without thermal differences between dense bed and freeboard (Chapter 3, the solid lines are the correlations found) and the other markers represent the experimental data obtained in the experiences of primary formation (diamond marker), secondary conversion (square marker) and the experiences with homogeneous temperature and 30% of steam in the inlet gas (triangle marker). The data from (Dufour et al., 2011) was also included in Fig. 4.10a (plus marker) for comparison.

The agreement of the experimental results with the correlation obtained in Chapter 3 was fairly good for the C_2H_2-Tar class 5 correlations (Fig. 4.10c). That means that even when the gasifier is thermally stratified and there is steam in the gas, it is possible to obtain a good estimation of the Tar class 5 concentration by measuring the C_2H_2 yield. However, larger scattering of data was found for the two other correlations (CH_4-benzene, CH_4-Tar class 4) particularly the one between benzene and methane. Hence, it can be concluded that thermal stratification and the presence of steam induced effects in the relative production of tars and hydrocarbons, lowering the accuracy of the two mentioned correlations when using them for tar estimation from light hydrocarbon measurements. Nevertheless, in spite of the dispersion found, the correlations presented in Chapter 3 give a rough estimation of the tar composition that could be useful for gas quality monitoring.

4. Conclusions

In this chapter the formation and secondary conversion of volatiles occurring during devolatilization of dried sewage sludge in fluidized bed were investigated. Additional tests were conducted to assess the influence of the DSS particle size on tar formation as well as to compare the results with wood. The experiences detailed in the present chapter extend the work initiated in Chapter 3 to specifically study the formation of tars and light hydrocarbons in thermally stratified systems produced by the staging of the fluidization agent.

On the basis of the main results obtained the following conclusions can be drawn.

- The increase in the dense bed temperature from 500°C to 800°C enhanced the production of light gas compounds, including light hydrocarbons, while the influence on tar yields is less significant. The yield of gravimetric tar was insensitive to the dense bed temperature between 500°C and 700°C, but it decreased 30 wt.% when the temperature was raised from 700°C to 800°C. The yields of Tar class 4 and 5 (light and heavy polyaromatic hydrocarbons) were hardly affected by the increase in the dense bed temperature from 500 to 800°C as a result of the small residence time of the volatiles in this zone. This occurred because in the tests conducted in the present work, the DSS particles were mainly decomposed near the bed surface. These results were not affected by the changes in the size of the DSS particle (from 1 mm up to 5 mm).

- The increase of the freeboard temperature from 600 to 800°C strongly enhanced the secondary conversion of volatiles, producing light gas and PAH due to the decomposition of primary tars.

- For a given freeboard temperature (higher than that in the dense bed) the fate of tars were mainly defined by the freeboard temperature, being rather insensitive to the dense bed temperature.

- DSS produces more tar (gravimetric and total CG-MS) than wood during devolatilization but the production of PAH (Tar class 4 and 5) was similar for both fuels. Furthermore, the variation trends of tars with the temperature of dense bed and freeboard were similar for both fuels, suggesting that similar conversion mechanisms occur during the conversion process, regardless of the parent fuel.

- The correlations between the yields of light hydrocarbon and tars obtained in Chapter 3 have shown to be roughly applicable also under conditions of thermal stratification and the presence of steam in the gas. Tar class 5 can be well estimated from C_2H_2 but the estimation of benzene CH_4 and Tar class 4 from CH_4 gives lower accuracy.

CHAPTER 5

Tar conversion over char

In the present chapter the influence of temperature, steam concentration and internal structure of the char on the rate of decomposition of toluene and naphthalene over various chars is studied. The kinetics of decomposition of the two tar compounds over three chars (commercial coconut and coal char, as well as char generated from DSS in our laboratory) were determined, accounting for char deactivation with time. The kinetics of DSS char is implemented in a previously developed model (Nilsson et al., 2012) to determine the effectiveness of tar reduction in the third stage of the FLETGAS gasifier described in Chapter 1.

1. Introduction

The removal of tars produced during gasification of biomass and waste has been extensively studied during the last decades (Abu el-Rub et al., 2004; Han & Kim, 2008; Devi et al., 2003). Both secondary measures converting the tar after the gasifier and primary methods aiming at minimizing tar production within the gasifier have been studied (Devi et al.,2003; Gómez-Barea & Leckner, 2009).

The search for an effective and cheap catalyst for the conversion of tars produced during biomass and waste gasification is one of the main tasks that should be addressed since the presence of tar compounds in the product gas is nowadays the main bottleneck for the commercial application of this technology. Recent publications have demonstrated the effectiveness of carbonaceous materials such as active carbon and biomass chars for tar conversion. This fact together with the low cost of the material (it is a by-product of solid fuel gasification) has increased the interest for using it as catalyst in novel gasifier designs.

Commercial activated carbon and char produced during biomass gasification have shown to have a catalytic activity for tar decomposition comparable to Ni-based catalysts (Abu el-Rub et al., 2008). The main advantage of the char as compared to other catalysts is that it is produced within the gasification process and its higher resistance to poisoning (Hosokai et al., 2008). A few pilot developments have been proposed using the char produced within the gasification process as catalyst for tar conversion (Brandt et al., 2000; Henriksen et al., 2006; van der Drift et al., 2005; Nilsson et al., 2012).

The activity of char for tar decomposition varies with the nature of the tar compound. On the one hand, tars with heteroatoms and aliphatic chains are converted faster than those containing pure aromatic rings (Griffiths & Mainhood, 1967). On the other hand, heavy tars are decomposed faster than light tars (Hosokai et al., 2008; Brandt et al., 2000; Griffiths & Mainhood, 1967; Matsuhara et al., 2010).

The ability of char to convert preferentially heavy poly-aromatic hydrocarbons (PAH) has been used to develop gas cleaning methods in systems burning the gas produced from biomass gasification in engines. These cleaning devices are mainly focused on lowering the gas dew point rather than reducing the total tar concentration in the product gas (Nilsson et al., 2012); since the gas dew point is mainly determined by the PAH concentration (van Paasen, 2004), the use of char seems to be a cheap and effective enough method for that application.

The main mechanisms involved during tar conversion over carbonaceous material are deposition, dehydrogenation (producing soot over the char surface) and gasification of the soot (Hosokai et al., 2008; Matsuhara et al., 2010; Hosokai et al., 2011; Sueyasu et al., 2012). These mechanisms are similar to those occurring during tar conversion over porous particles (Ito et al., 2003; Namioka et al., 2003; Hosokai et al., 2005; Matsuoka et al., 2006; Kuramoto et al., 2009). The main difference of carbonaceous materials derived from biomass with respect to other porous materials, such as zeolites or γ-alumina, is that the former contains alkaline and alkaline-earth metallic (AAEM) species that may act as catalysts of the steam gasification reaction both over the carbon in the char and in the soot. This is useful because, under certain operating conditions, the deactivation process can be effectively reduced by the simultaneous consumption of the soot formed over the porous char (Matsuhara et al., 2010; Hosokai et al., 2011; Sueyasu et al., 2012).

The rate of homogeneous reforming of aromatic tar below 900-1000°C (Jess, 1996) is small compared to heterogeneous conversion over carbonaceous surfaces (Abu el-Rub et al., 2008). It has been found that reforming of aromatic molecules, such as benzene and naphthalene, over char does not produce other aromatic compounds, i.e. aromatic molecules decompose into soot and light gas but do not produce other tar compounds (Hosokai et al., 2008). In contrast, alkyl-aromatics and heteroatomic-aromatic compounds may produce lighter tars by dealkylation and decarboxylation (Griffiths & Mainhood, 1967).

Kinetic expressions for the rate of tar conversion over char have been published. First order kinetics with respect to tar concentration in the gas was determined for the rate

of conversion of naphthalene and toluene over biomass char (Abu el-Rub et al., 2008; Juneja et al., 2010). Table 5.1 presents the kinetic parameters obtained in both studies. These expressions allow estimation of the initial rate of naphthalene and toluene conversion over fresh biomass char (initial conversion) but deactivation of the char with time is not included. Since deactivation is the main practical limitation for the use of catalytic materials, such information should be included in kinetics models for the assessment of commercial processes (Gómez-Barea et al., 2012).

The first attempt for the simulation of the char moving bed (third stage) of the FLETGAS gasifier was made (Nilsson et al., 2012a) by calculating the rate of tar conversion over char from the kinetics for wood char presented by (Abu el-Rub et al., 2008). The main conclusion was that the heavy tar is effectively converted in the moving char under the operation conditions of the FLETGAS gasifier (Nilsson, 2012). However the kinetics used correspond to a different char and deactivation of the char was not taken into account in the reaction model, making the results of the simulations questionable. Validation of the results published by (Nilsson, 2012) is carried out at the end of this chapter.

Table 5.1: Activation energy and pre-exponential factor for tar conversion over char; commercial biomass char for naphthalene conversion (Abu el-Rub et al., 2008) and wood char for toluene conversion (Juneja et al., 2010).

	E_a (KJ/mol)	k_0 (s^{-1})
Kinetic equation	$-r_{tar} = k_0 \exp\left(-E_a / (RT)\right) C_{tar}$	
Naphthalene	61	$1 \cdot 10^4$
Toluene	81.6	$1.8 \cdot 10^4$

A few works have been published dealing with deactivation of char during tar conversion (Hosokai et al., 2008; Matsuhara et al.,2010; Hosokai et al.,2011), one of them studying specifically the influence of the internal structure of the char on tar conversion (Hosokai et al., 2008). During tests conducted in fixed char beds, the conversion of tar in the gas was found to decrease with time when no steam was added to the inlet gas. In addition, a decrease in the micropore surface area of the char during the test was measured. It was then postulated that the micropores provide the sites for reaction, which deactivate by coking. A kinetic expression taking into account these observations was proposed (Hosokai et al., 2008). Additional tests using steam in the gas were found to increase the activity of char, suggesting that soot deposits are gasified by steam creating new micropores (Hosokai et al., 2008; Hosokai et al., 2011).

The present chapter investigates the effects of temperature and steam concentration in the gas on the rate of toluene and naphthalene decomposition over three chars having different internal structure. Special attention was paid to evaluate the char

deactivation and the evolution of the internal structure with time, as well as to obtain kinetic expressions for the simulation of the process.

As it was commented in Chapter 2, the method for char preparation has a great influence on its reactivity. Therefore to test the actual activity of char for tar conversion in the third stage of the FLETGAS gasifier during operation with DSS, the kinetics of the DSS char should have been studied by generating the char in similar conditions to the FLETGAS gasifier, i.e. FB conditions and without cooling the char down to room temperature. This is a limitation of the present work that should be addressed in the future as it is discussed in Chapter 6. Nevertheless, this work is a step forward as the activity of the DSS char for tar reforming is analyzed and compared with other two chars, so the preliminary ability of DSS char for tar conversion is evaluated as well as the deactivation process, which is not expected to vary significantly with the form of char preparation.

2. Experimental procedure

Before each test the reactor was loaded with dry char and was heated up to 950°C under N_2 atmosphere. Some gas was emitted during the heating period, which slightly varied with peak temperatures for a given char. In order to apply equal method of preparation for all tests using the same char, the peak temperature was set at 950°C for 5 minutes and thereafter the desired test temperature (750, 850 or 950°C) was established. The mass loss measured during the heating period was 6.6% for the coal char, 4.2% for the coconut char and 5.5% for DSS char. It was verified that the internal structure of the chars did not vary significantly during the heating period.

Once the test temperature was reached, feeding of the gas with the desired composition (N_2, H_2, H_2O and tar mixture) began. The total duration of each test was 75 minutes, during which three tar samples were taken at different times (t_{ex}). During each tar sampling two gas samples were taken by using gas-tight syringes.

At the beginning of the test, the gas flowrate was adjusted to set a gas residence time in the char bed (τ) of 0.1 s. The gas flowed through the gas cleaning line during this period. Before the tar sampling, the gas flowrate was decreased to give τ=0.3 s. After two minutes of steady flow at τ=0.3 s the sampling line was switched on and the gas was driven to the tar sampling train. The tar sampling lasted five minutes, after which the gas from the reactor was directed again to the cleaning line, adjusting the gas flowrate to give τ=0.1 s once again. After the last sampling of the test the char bed was cooled down in N_2. The spent char was weighed and stored for the porosimetry analysis.

The residence time of the gas in the char bed of 0.3 s during the sampling period was applied in order to achieve significant conversion of tar, whereas the lower τ (τ=0.1 s) was applied during the rest of the test in order to minimize the variation of activity along the char bed. In this way, the gas was ensured to flow through a char bed with nearly uniform activity at any time t_{ex} (note that the activity changes with time t_{ex}

during the test, but at any t_{ex}, the activity is expected to be the same along the char bed). This way of operation ensured better measurements for the determination of kinetics.

Table 5.2 summarizes the experimental conditions tested. The first set of experiments (tests 1-9) aims at determining the influence of temperature and the internal structure of the char on tar conversion as well as to study the loss of activity of char with time. The kinetics was determined using these data. The second set of experiences (10-15 tests, together with 1-3) was carried out to specifically study the combined effects of steam concentration and temperature on the deactivation of coconut char. The tests 1-3 have been written again in the second part of the table to allow easier comparison of the tests with different steam concentration.

Table 5.2: Operational conditions of the tests. In all tests the concentrations of toluene and naphthalene in the inlet gas were 12 and 8 g/Nm^3, respectively and that of H_2 was 8% v/v, and the gas residence time in the char bed during tar sampling was τ=0.3s.

	Conversion over different chars								
Id. Test	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Char type	**Coconut char**			**Coal char**			**DSS char**		
Temperature (°C)	750	850	950	750	850	950	750	850	950
N_2 in the feeding stream (% v/v)	77	77	77	77	77	77	77	77	77
H_2O in the feeding stream (% v/v)	15	15	15	15	15	15	15	15	15
	Effect of steam concentration								
Id. Test	**10**	**1**	**11**	**12**	**2**	**13**	**14**	**3**	**15**
Char type	**Coconut char**								
Temperature (°C)	750	750	750	850	850	850	950	950	950
N_2 in the feeding stream (% v/v)	92	77	67	92	77	67	92	77	67
H_2O in the feeding stream (% v/v)	0	15	25	0	15	25	0	15	25

3. Results and discussion

3.1. Conversion of tars over different chars

The catalytic conversion of toluene and naphthalene over the three chars as a function of test time is presented in Fig. 5.1 for temperatures between 750°C and 950°C (tests 1-9 in Table 5.2). The conversion measured during the tests using a bed of silicon carbide (CSi) is also included in the figure. It was found that tar conversion over CSi does not change with time so the results from these tests are indicated by the horizontal lines in the figure. The values of conversion of toluene and naphthalene over CSi at 950°C are not visualized in the figure (the two graphs at the bottom), because they are lower than the minimum one represented with the scale chosen, being their respective values, 0.79 and 0.72.

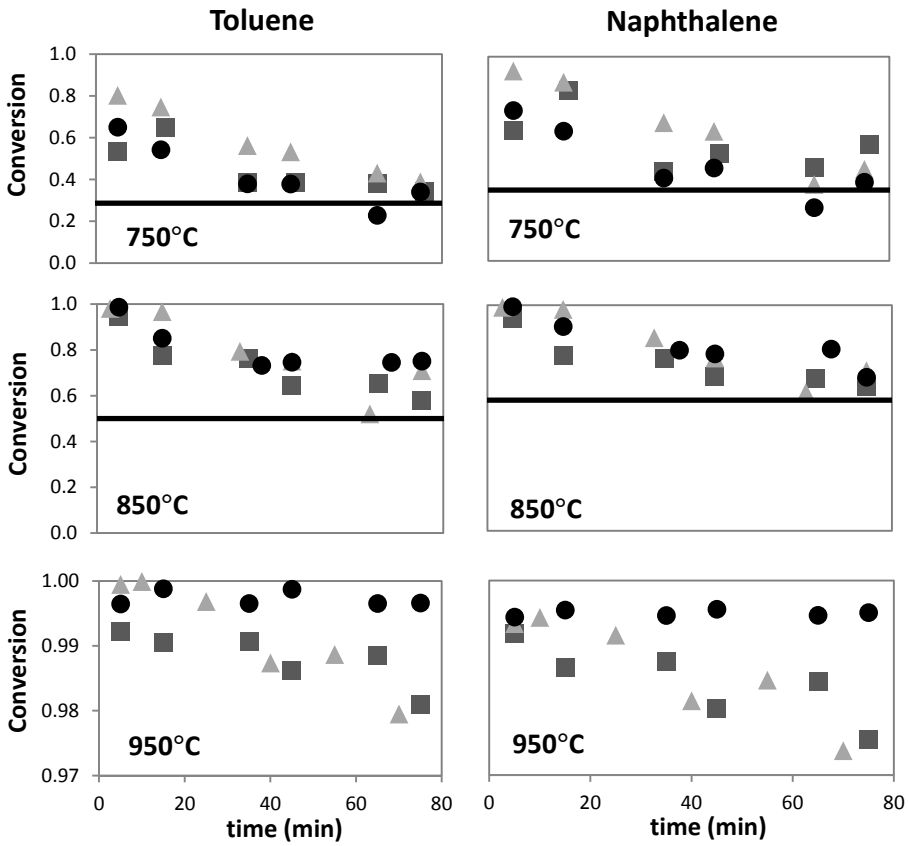


Fig. 5.1. Conversion of toluene and naphthalene as a function of test time for various temperatures and type of char. 15% of steam in the carrier gas; ●: coal char, ▲: coconut char, ■: DSS char. Horizontal lines represent tar conversions over CSi.

In spite of the different internal structures of the three chars employed (see Table 2.4), the evolution of conversion with time is seen to be similar for the three chars. At 750°C coconut char gave the highest tar conversion for the entire test time, whereas coal char was the most active char at 950°C, maintaining the initial activity for the entire test. The conversion of both tars is almost complete at the beginning of the test at temperatures above 850°C for the three chars tested, whereas at 750°C complete conversion is not achieved, not even at the initial time. At 750°C toluene is slightly less converted than naphthalene regardless of the char employed, although this difference is lower at higher temperature, where both tars achieve similar conversions.

Continuous deactivation of the char with time is observed during tests at 750°C and 850°C, where the conversion over char is similar to that over CSi after 70-80 minutes, indicating almost complete deactivation of the char. The evolution of conversion at 950°C is drastically different as the conversion of the two tars over the three chars remains roughly constant during the whole test (note the scale of the graphics at 950°C). It is concluded that increasing the temperature not only leads to higher tar

conversion but also to lower char deactivation. The reason for this is discussed in Section 3.2 where the simultaneous effects of temperature and steam concentration in the gas are analyzed.

Table 5.3 presents the properties characterizing the internal structure of char and the weight balance of the char beds, this latter defined as the increase in weight of the char bed during the test (75 min). According to (Hosokai et al., 2011), the weight balance is a measure of the difference between the rates of tar deposition and carbon gasification. Following this interpretation, positive weight balance indicates that the rate of tar deposition on the char surface (forming soot) is faster than the carbon (soot and char) gasification by steam and vice versa. The results in Table 5.3 point out that whereas the internal structure of DSS char is hardly influenced by the temperature, that of coconut and coal chars are strongly affected by the test temperature. For these two chars the total surface area and the micropore surface area were reduced during the test at 750°C and 850°C, while at 950°C these parameters are higher for the spent char than for the fresh char. These results are consistent with a mechanism of reaction given by tar deposition (with dehydrogenation) followed by soot gasification (Hosokai et al., 2008): at 750°C and 850°C the deposition rate is higher than the soot gasification rate, leading to the blocking of char pores with time due to soot deposition and the increasing in bed weight. In contrast, the decrease in the bed weight with time observed at 950°C reveals that the rate of carbon (char and soot) gasification is higher than that of coking, increasing the porosity of the char. The small variation of the char structure in the tests with DSS char could be attributed to the high ash content in this material (84.8 wt%), being its internal structure less affected by the conversion processes compared to the other two chars. Overall, the results presented highlight the correlation between the weight balance (carbon balance) and the char bed deactivation: the tests with negative weight balance present negligible decrease in activity, whereas loss of activity with time is related with tests presenting positive weight balance. The small differences observed in tar conversion and char deactivation for the three chars suggest that the internal structure of the fresh char is not straightforwardly related with the char activity. Instead of the internal structure, other parameters such as the concentration of AAEM compounds on the char surface may influence the char activity (Sueyasu et al., 2012).

The dry gas volumetric fractions of hydrogen and carbon monoxide measured for the test using different chars and temperatures are shown in Fig. 5.2. The volume fraction of both species decreases with time, being the trends similar for the three chars. A significant drop in H_2 concentration (and CO to a lesser extent) is observed during the initial stages of the test using DSS char (first squared point in the various graphs of Fig. 5.2). The observed decrease in CO with time during the test is due to the char deactivation as a result of the decrease in the carbon gasification rate (reaction 5.1). The significant increase in CO with temperature indicates an increase in the carbon gasification rate. The increase in H_2 is the result of the enhancement of both carbon gasification and tar coking (reactions 5.1 and 5.2).

$$C + H_2O \rightarrow CO + H_2 \quad (5.1)$$

$$\text{Tar} \rightarrow C\ (\text{soot or coke}) + H_2 \quad (5.2)$$

Table 5.3: Internal structure of spent chars and their weight change after 75 min of test (Tests 1-9).

	Total surface area (BET) (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Macropore volume (cm^3/g)	Porosity (%)	Bed weight balance* (g)
Coc. char 750°C	435	348	0.20	0.055	0.066	13.5	+10.57
Coc. char 850°C	484	397	0.22	0.069	0.074	16.5	+5.93
Coc. char 950°C	677	540	0.30	0.104	0.088	19.1	-12.46
Coal char 750°C	264	111	0.06	0.141	1.635	68.3	+4.60
Coal char 850°C	269	123	0.07	0.126	2.020	72.5	+4.39
Coal char 950°C	916	512	0.29	0.062	2.633	69.9	-14.20
DSS char 750°C	65	14	0.01	0.093	0.460	55.8	+0.03
DSS char 850°C	41	4	0.00	0.083	0.436	54.7	+0.90
DSS char 950°C	55	8	0.00	0.089	0.477	57.3	-4.51

*Discounting the weight loss due to the initial heating to 950°C

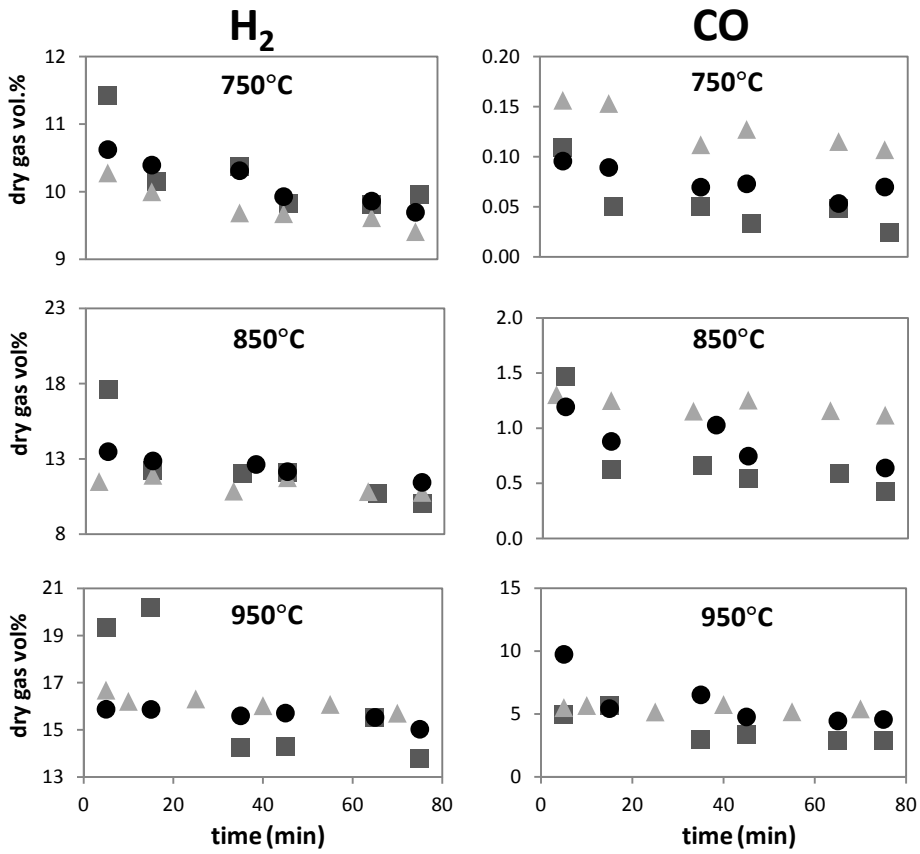


Fig. 5.2. Hydrogen and carbon monoxide molar fraction in the exit gas as a function of test time for various temperatures and type of char; ●: coal char, ▲: coconut char, ■: DSS char

The lower gasification rate with time is due to the continuous increase in the proportion of carbon coming from the soot on the char surface (the rest of carbon on the surface is that of the original char), which makes the overall gasification rate lower as the deposition proceeds, since the reactivity of carbon in the soot is lower than that in the original char (Zhang et al., 2010). This is understood if one compares the results obtained here (with tar in the gas leading to soot deposition) with those that would have been obtained in a test where tar is not present in the gas, i.e. only gasification of the carbon in the original char would occur. In such a case CO would be produced by char gasification at roughly constant rate until a high degree of conversion (this is a usual characteristic of most chars, presenting a constant gasification rate up to 70-85%, (Hosokai et al., 2008). The drop in H_2 with time is probably due to the combined effects of the decrease in the rates of carbon gasification and tar polymerization over the char surface.

3.2. Influence of steam concentration

The results presented in Section 3.1 were based on tests conducted with 15 vol% of steam in the gas. In this section the steam concentration is varied between 0 and 25 vol% to determine its influence on tar conversion rate and on char deactivation. The tests have been conducted using coconut char only. Fig. 5.3 displays the evolution of tar conversion with time for the tests varying the concentration of steam in the inlet gas (0, 15 and 25% v/v) and temperature (750, 850 and 950°C) for coconut char. The corresponding char weight balance and total surface area for these tests are presented in Fig. 5.4.

As seen in Fig. 5.3 the influence of steam on the conversion rate of the two tars is only significant at 950°C, particularly as steam concentration is raised from 0 to 15%. At 750°C and 850°C the coconut char is deactivated regardless of the concentration of steam. After 60 minutes, the tar conversion is seen to reach the value measured using CSi. In contrast, at 950°C the char is deactivated only when steam is not present in the gas. It is observed that the initial activity of the char is maintained over the entire test when steam concentration is 15% and higher.

It is seen in Fig. 5.4 that the influence of steam concentration on the total surface area and bed weight balance depends on the temperature: almost no influence is seen at 750°C (first two graphs at the top), whereas the influence is significant at 850°C and 950°C. At 850°C, there is an increase in total surface area and a decrease in bed weight as the steam concentration is raised (see two graphs at intermediate level in Fig. 5.4). At 850°C it is noteworthy that despite the differences in the total surface of the spent char at different steam concentrations, the tar conversion is not affected (see Fig. 5.3), indicating that there is not a direct relation between the char internal structure and tar conversion and so that other phenomena affect the number of active sites available for reaction. At 950°C with 15% or 25% of steam in the gas (see two graphs at the bottom in Fig. 5.4), the negative bed weight balance is accompanied by a net increase in total surface area of the char during the test, indicating that there is a loss of carbon from the original char. For these two tests the char maintains the initial activity as shown in Fig. 5.3.

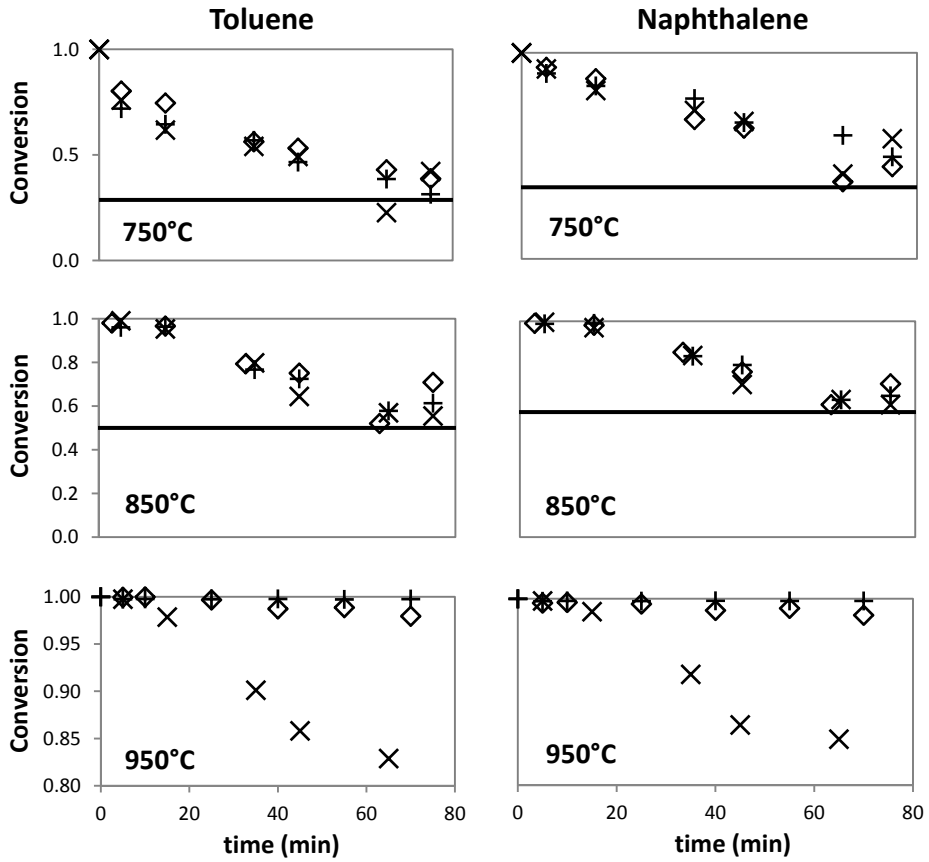


Fig. 5.3. Conversion of toluene and naphthalene over coconut char bed as a function of test time for various temperatures and steam concentrations; ×: 0% of steam, ◇: 15% of steam, +: 25% of steam.

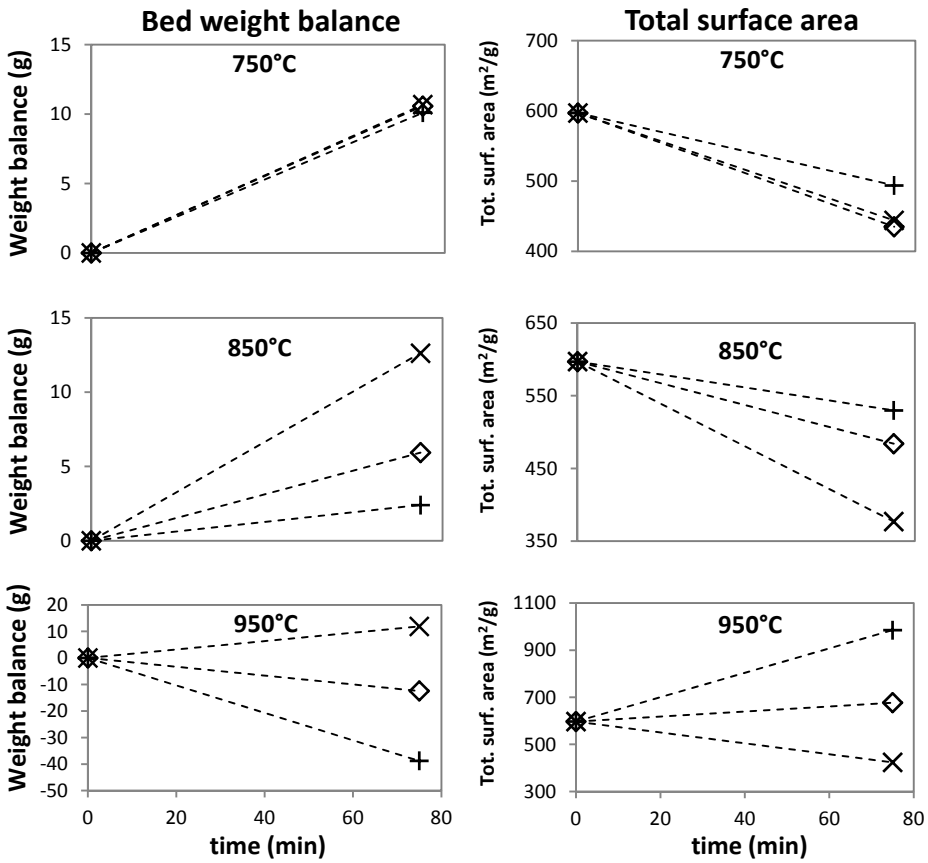


Fig. 5.4. Total surface area and bed weight balance as a function of test time for various temperatures and steam concentration: ×: 0% of steam, ◇: 15% of steam, +: 25% of steam.

3.3. Mechanism of tar conversion over char surface

Fig. 5.5 summarizes the conversion mechanism consistent with the observations discussed. Initially the tar compounds meet a fresh char containing certain number of active sites distributed over the surface. The tar is adsorbed on the char structure and undergoes polymerization reactions, producing hydrogen and soot, the latter remaining on the char surface as solid deposits. This soot blocks the active sites, hindering the interaction of the active sites with the gaseous tar. If the rate of carbon deposition is higher than that of carbon consumption by gasification, accumulation of soot over the surface occurs, decreasing the number of active sites available for reaction with tar molecules and then the char activity. This occurs for the three chars investigated at temperatures of 750 and 850°C regardless of the steam volume fraction and at 950°C when steam is not present in the gas. The active sites could be attributed to the presence of AAEM species in the fresh char since these species are

known to be active during steam gasification of soot generated after tar deposition on char surfaces (Sueyasu et al., 2012).

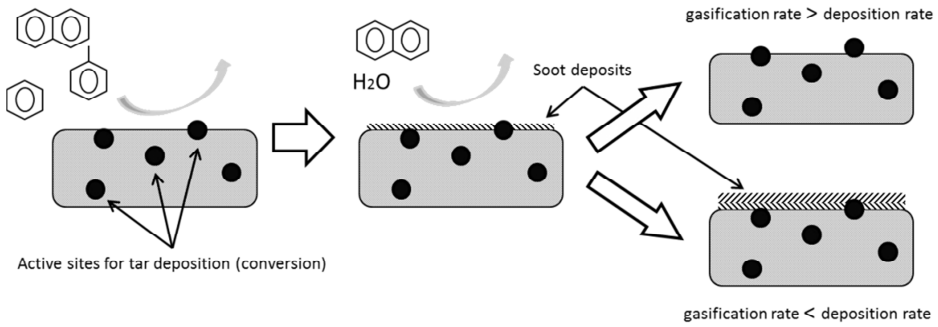


Fig. 5.5. Representation of the mechanism for tar conversion over carbonaceous surface.

3.4. Kinetic modeling of tar conversion over different chars

3.4.1. Kinetic model

The conversions of toluene and naphthalene over the chars tested with a constant steam concentration in the gas of 15 % were used to determine the kinetics of conversion over the different chars accounting for the deactivation process with time. The steam concentration selected is that typically contained in the gas produced from air-blown biomass gasifiers, so the kinetics obtained is useful to assess the performance of a char bed treating a gas from this process (Nilsson et al., 2012). The rate of tar conversion over char was assumed to follow first order kinetics with respect to tar concentration. The deactivation of char was modeled by introducing an activity factor, *a*, which varies with time (*a*=1 fresh char with full activity; *a*<1 char partially deactivated). Taking into account these assumptions, the kinetic equation for the tar decomposition is written as

$$-r_{tar} = k\, C_{tar}\, a \tag{5.1}$$

being *k* the rate coefficient and C_{tar} the tar concentration. The activity *a* is defined as

$$a = \frac{-r_{tar,t}}{-r_{tar,0}} \tag{5.2}$$

where $-r_{tar,t}$ and $-r_{tar,0}$ are the reaction rates at time t and the initial rate, respectively. The initial time was set to the beginning of the first sampling period (5 minutes after the gas feed was initiated). Assuming plug flow of the gas through the char bed, the rate coefficient, *k*, can be obtained by integration from 0 to the gas residence time in the char bed τ.

$$k = \frac{-\ln(1-\chi)}{\tau} \tag{5.3}$$

where χ is the tar conversion defined in (Eq. 2.1, Chapter 2) as

$$\chi = \frac{(C_{tar,in} - C_{tar,out})}{C_{tar,in}} \tag{2.1}$$

$C_{tar,in}$ and $C_{tar,out}$ are the inlet and outlet tar concentrations respectively. The gas residence time in the char bed was calculated with respect to the empty char bed volume, i.e. the reactor volume divided by the total gas flow at the bed temperature.

The tar conversion, χ, calculated from Eq. (2.1) for samples taken at different times, $t_{ex,}$ was fitted to a continuous function to estimate χ at different t_{ex} from 5 to 75 minutes.

The kinetics was obtained in two steps: First the data derived for the initial time (t=5 min) were employed to obtain the rate coefficient, k, in Eq. (5.1) and then the activity as a function of the time of reaction was determined.

Assuming that k follows the Arrhenius' law (Eq. 5.5), the frequency factor k_0 and activation energy E_a were obtained.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{5.5}$$

The activity as a function of time was fitted to the following empirical expression

$$a = \frac{1}{1 + k_d t_{ex}^p} \quad \text{with} \quad p = p_1 + p_2 T^* \tag{5.6 and 5.7}$$

where k_d, p_1 and p_2 (Eq. 5.7) are empirical parameters to be fitted and T^* is a normalized temperature defined as T_b(K)/1023. k_d could be interpreted as a deactivation coefficient but nonetheless Eq. (5.6) is an empirical expression without any fundamental basis (it was applied because it fits the measurements well). A kinetics based on more fundamental steps derived from the present study is under development.

3.4.2. Kinetic modeling results

The method above described was applied to obtain the kinetics for the rate of reaction of toluene and naphthalene over the three chars employed. The tests used were 1-9 (see Table 5.2).

The kinetics of the initial rate of reaction (at t=5 min, the time for the first measurement) is given by Eq. (5.1) with a=1 and the kinetics coefficient k given by Eq. (5.5). Table 5.4 presents the kinetic parameters that best fit the experimental data for the decomposition of the two tar compounds over the three chars. The correlation factor (R^2) between the experimental and the kinetic model conversions is also reported.

Table 5.4. Kinetic parameters for the empirical expression given for the rate of decomposition of the two tars over the three chars (E_a Activation energy; k_0 frequency factor).

Kinetic equation

$$-r_{tar} = k_0 \exp\left(-\frac{E_a}{RT}\right) C_{tar} \left(\frac{1}{1+k_d t_{ex}^{\,p_1+p_2\left(\frac{T}{T_0}\right)}}\right)$$

	Coal char		Coconut char		DSS char	
	Toluene	Naphthalene	Toluene	Naphthalene	Toluene	Naphthalene
k_0 (s^{-1})	$1.8\cdot10^{5}$	$2.2\cdot10^{4}$	$4.1\cdot10^{4}$	$5.3\cdot10^{4}$	$9.5\cdot10^{4}$	$7.6\cdot10^{3}$
E_a (KJ/mol)	91	71	75	72	88	63
k_d (s^{-p})	$3.6\cdot10^{-3}$	$1.1\cdot10^{-3}$	$3.8\cdot10^{-3}$	$1.1\cdot10^{-2}$	$1.6\cdot10^{-3}$	$3.8\cdot10^{-3}$
p_1	2.13	2.68	1.15	0.74	1.45	1.48
p_2	-1.32	-1.68	-0.35	0	-0.65	-0.77
R^2	0.96	0.92	0.82	0.78	0.90	0.74

Fig. 5.6 compares the toluene and naphthalene conversion attained using the kinetics obtained for the three chars without deactivation (initial conversion). The conversions are plotted as a function of the gas residence times in the char bed τ for three temperatures. The conversions calculated using the kinetics obtained in another work for commercial biomass char ((Abu el-Rub et al., 2008; Juneja et al., 2010), see Table 5.1) are also included. It is concluded that: (i) The activity reported by (Juneja et al., 2010) for toluene conversion over wood char is clearly lower than the activities for different chars reported by the present work. (ii) The activity of coconut char to decompose the naphthalene is similar to that of commercial biomass char, both being slightly more active than DSS and coal chars. (iii) Whereas the gas residence time in the char bed needed to completely convert the tar at 850°C is about 0.3 s, it can be decreased to 0.2 s at 950°C. (iv) At the lowest temperature (750°C) naphthalene is converted slightly faster than toluene, while the difference is negligible at higher temperatures. Note that these conclusions apply for char without deactivation.

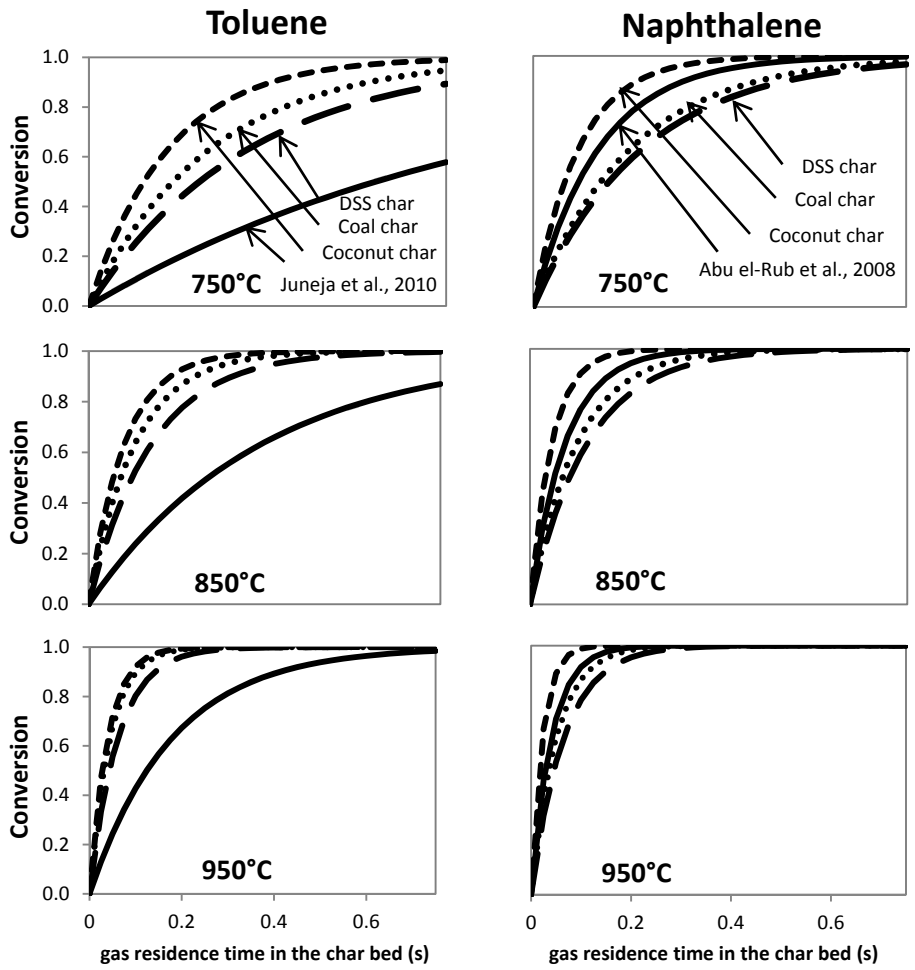


Fig. 5.6. Toluene and naphthalene conversion as a function of gas residence time τ for the three chars studied at initial time (with fresh char), calculated from the kinetics given in Eq. (1) and that calculated for char from biomass ((Abu el-Rub, 2008; Juneja et al., 2010), see kinetics in Table 5.1) at 750°C, 850°C and 950°C

Fig. 5.7 presents the experimental activity at different times for the three chars and the two tar models. Equal marks in the graphs correspond to a constant temperature. The figure shows that the activity decreases with time for all chars and tars. Moreover, for a given char and tar the higher the temperature, the lower the deactivation of the char with time. It is remarkable that the loss of activity for coconut char is only slightly affected by temperature, particularly for naphthalene.

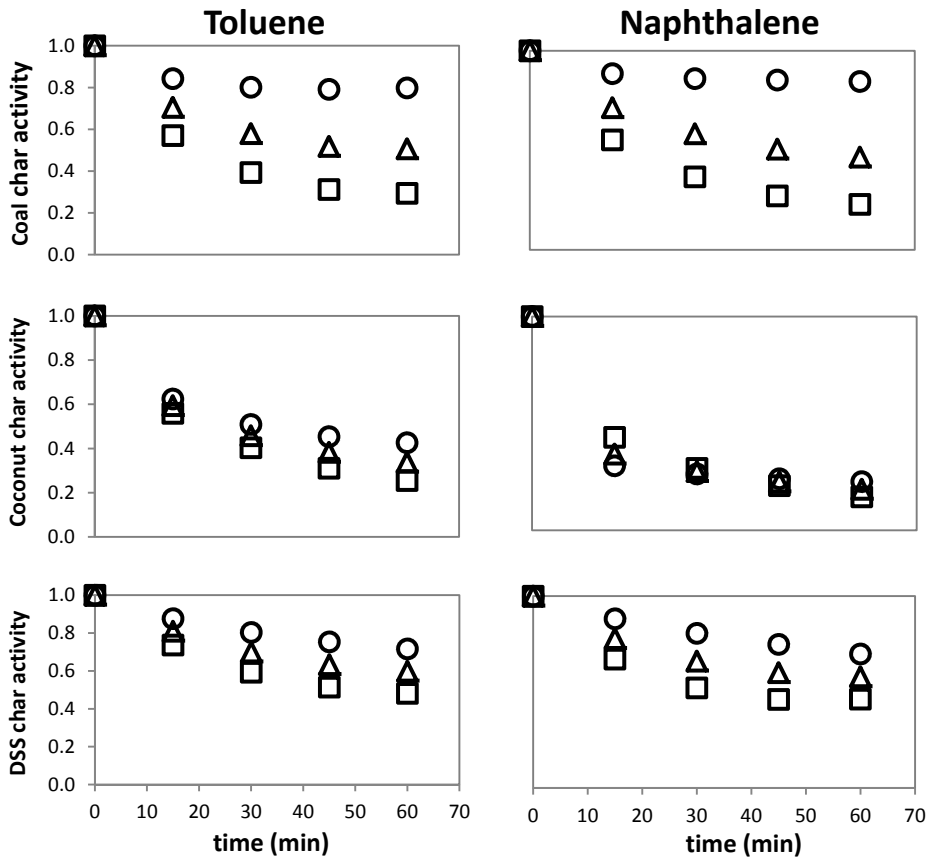


Fig. 5.7. Evolution of the catalytic activity of the char with the test time for various temperatures; □: 750°C, △: 850°C, ○: 950°C.

Fig. 5.8 compares the experimental and predicted conversions for toluene and naphthalene over coal char at the three temperatures, showing that the agreement between experiments and model is fairly good. Fig. 5.9 presents the model and measurements for all operating conditions (tar model, char type, temperature and test time). The dispersion is mainly due to the experimental uncertainties of the measurements, as it was already evident from the data presented in Fig. 5.1, where significant dispersion of the conversion measurements at different times was observed. Despite the dispersion, the kinetics fits reasonably well the trends given by the measurements under different conditions, being most data within the ±20% of error (dotted lines).

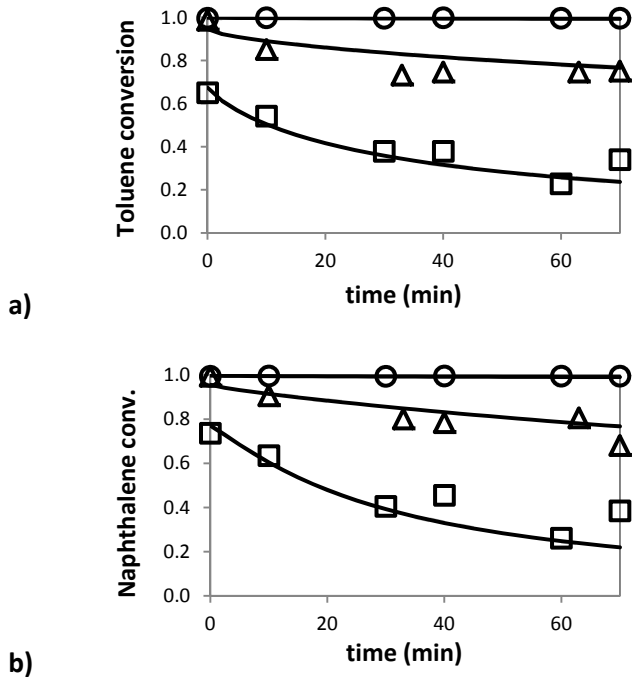


Fig. 5.8. Comparison between experimental (markers) and model (solid lines) conversion for various temperatures; □: 750°C, △: 850°C, ○: 950°C. (a) coal char conversion for toluene; (b) coal char conversion for naphthalene.

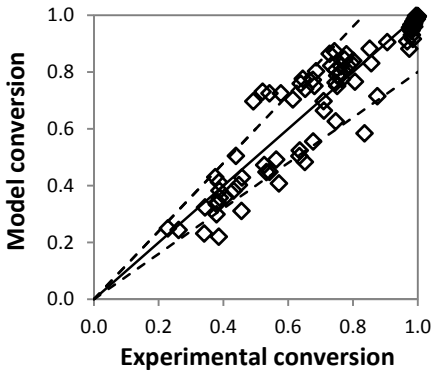


Fig. 5.9. Comparison between the tar conversion measured and that obtained from the kinetic model. Dotted lines represent deviation of ±20% between experimental and model data.

3.4.3. Simulation of the moving bed of DSS char in the FLETGAS gasifier

Simulations of the FLETGAS gasifier were made in Nilsson et al. (2012a) to investigate the effect of different parameters when processing DSS. The third stage (moving bed

of char) was simulated employing the kinetics of tar conversion obtained for a commercial biomass char (Abu el-Rub et al., 2008), where char deactivation was not taken into account. Under the conditions tested, almost complete conversion of heavy tars (taking naphthalene as model tar) was calculated (Nilsson et al., 2012).

In this section, the model of Nilsson et al. has been modified by implementing the kinetics for naphthalene over DSS char obtained in this chapter to simulate the third stage of the FLETGAS gasifier. The Case 3.2 in Nilsson et al. (2012a) is taken as base case to discuss the performance of the gasifier. The box in the dotted line in Fig. 5.10 defines the control volume where the tar is converted over char. The main inputs and process parameters (temperature and flowrates) calculated for the simulated case are shown in Fig. 5.10. The char flowrate entering the moving bed is 14 kg/h and the gas flowrate 44 Nm^3/h; the internal diameter of the moving bed is 0.3 m. The moving bed is chosen long enough to analyze the results at different positions along the bed (note that the gas and solids are assumed to move down in plug flow and then the total length of the bed does not affect the results upstream). The overall equivalence ratio of the system, defined as the ratio of the oxygen fed and that for stoichiometric combustion of the fuel, is 0.27. The SOR, defined as the mass ratio between the steam and the oxygen fed to the gasifier, is 0.24.

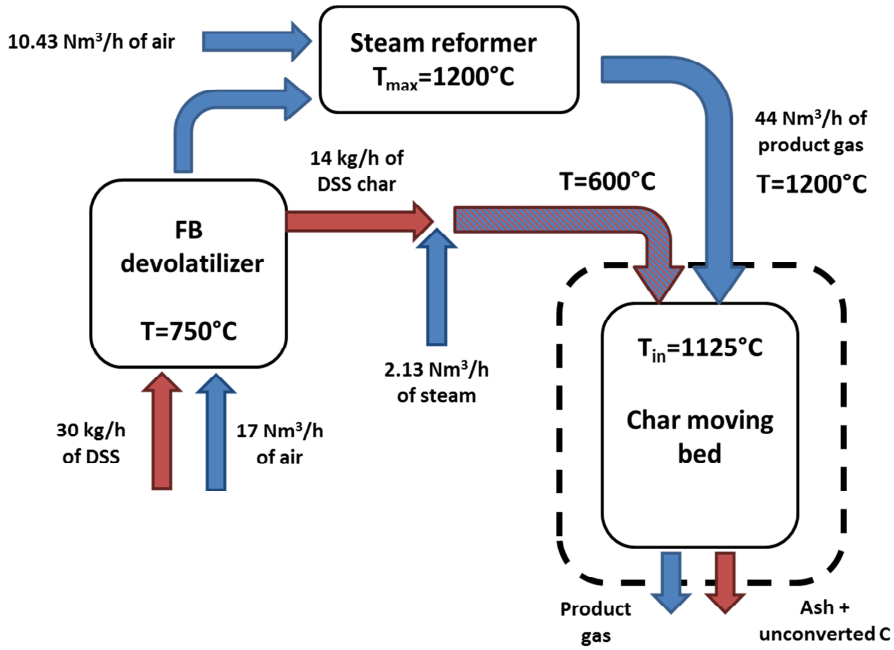


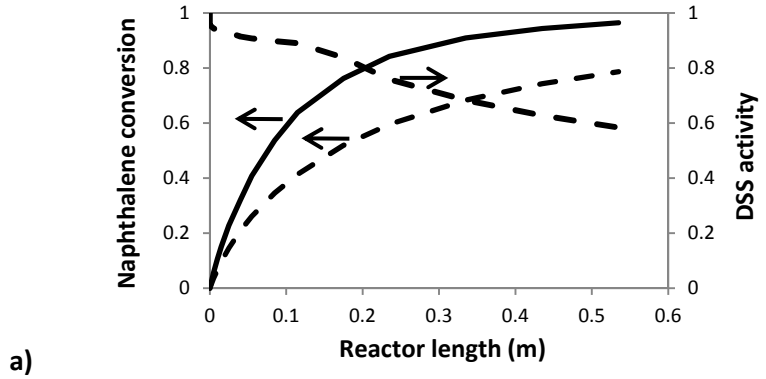
Fig. 5.10. Simulated gasifier conditions corresponding to Case 3.2 from Nilsson et al., (2012a). The dotted box surrounds the control volume containing the moving char bed, where the new kinetic for tar conversion over DSS obtained in this work has been implemented. Simulations have been conducted with the model of Nilsson et al. (2012a)

The profiles of various parameters along the moving bed are plotted in Fig. 5.11a–d: naphthalene conversion and activity of the DSS char (Graph a), char conversion and the bed temperature (Graph b) and gas residence time and molar fraction of steam (Graph c). It is observed that the calculated naphthalene conversion with the DSS char kinetics is lower than that reported by Nilsson et al. (2012a) using the kinetics from Abu el-Rub et al. (2008). This is explained by the lower rate of naphthalene conversion over DSS char compared to that over the biomass char tested by Abu el-Rub et al. (2008) (see Fig. 5.6). In addition, the DSS char deactivates significantly along the bed (see Fig. 5.11a), particularly after 0.1 m from the entrance. It is seen that the activity of the char is below 60% after 0.5 m from the entrance. It is concluded that to achieve high conversions of naphthalene with the DSS char it is necessary to increase the bed length, i.e. the gas residence time, even at the expense of having a significantly less active char (less than a half with respect to that at the entrance of the moving bed). Nevertheless, as commented in the introduction of the present chapter, the conversion rate over char depends on the molecular weight of the tar compound, which is higher with heavier molecules. Then, since the naphthalene is the lightest PAH, i.e. the less reactive of the PAH, it is expected that most of the heavy PAH are converted in the DSS char bed effectively, reducing the tar dew point of the product gas down to the required specification.

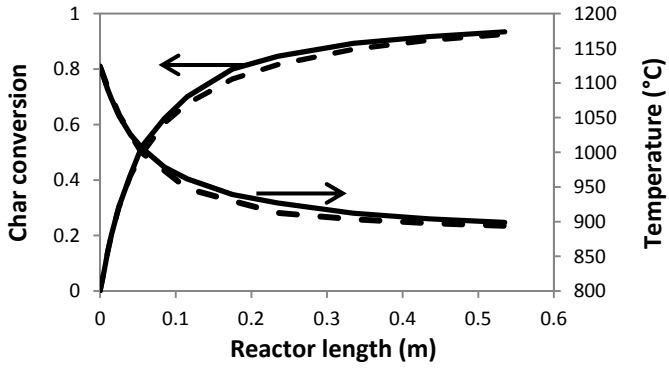
It is observed in Fig. 5.11b that the change in the kinetics of tar has a minor effect on char conversion since the kinetics of char used in the present simulation was the same as that presented in (Nilsson et al., 2012a). However, as it was previously mentioned in this chapter, the tar conversion might influence the rate of char conversion since the soot deposited may cover the carbonaceous surfaces of the original char. Although the gasification of the soot is also occurring in parallel with deactivation, it is not modeled in the current simulation to calculate the char conversion along the bed. Hence, the char conversion in the real process could be lower than that predicted by the simulation. Since the soot is carbon and is lumped with the original char, the carbon content in the solids of the outlet stream would be higher than that calculated. This is an important consideration that needs to be addressed for the development of FLETGAS process if high carbon conversion has to be achieved.

Fig. 5.11c presents the relation between the bed length and the gas residence time in the bed for the simulation made. Comparing the results of Fig. 5.11a with that of Fig. 5.11c it is observed that a residence time of 0.4 s is necessary to achieve a naphthalene conversion of 0.7. It is seen that the steam molar fraction is 21% at the inlet, dropping to 12% at the outlet. As the kinetics of DSS used in the simulations is strictly valid for 15% of steam in the gas, the results have to be taken with caution because the effect of steam on the kinetics of tar conversion over DSS was not analyzed in this work. However, the effect of steam over coconut char activity was investigated (see Section 3.2 of the present chapter) and, in spite of the differences in the char structure, similar tendencies are expected with both types of char. For coconut char the tar conversion was hardly affected by the steam concentration in the range 15-25 vol% maintaining the bed at 950°C. Then it can be concluded that, due to the high temperatures in the bed (see Fig. 5.11b) and the range of steam concentrations (21-12%), the kinetics used is roughly valid. In a longer reactor where the decrease in steam would be more significant, the deactivation calculated with the

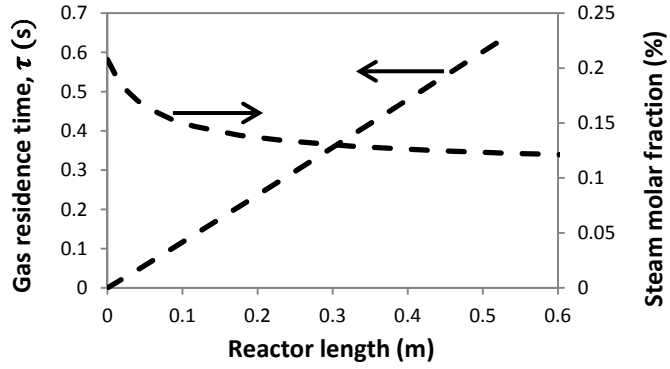
kinetics implemented would lead to higher rate of naphthalene conversion than the actual one, and so the calculated conversion would be questionable. Various measures can be done in the FLETGAS process to increase the steam concentration at the entrance of the moving bed as discussed in Chapter 6.



a)



b)



c)

Fig. 5.11. Profiles along the bed of various parameters: Naphthalene conversion and activity of the DSS char (a); Char conversion and bed temperature (b); Gas residence time (τ) and molar fraction of steam (c). Solid lines are results from (Nilsson et al., 2012a) using kinetics from literature (for biomass char), whereas dotted lines are results obtained with the kinetics of tar over DSS char obtained in the present thesis.

4. Conclusions

In this chapter the effectiveness of three types of char for toluene and naphthalene conversion was studied at different temperatures (750–950°C) and steam molar fractions (0–25 vol%), taking char deactivation into account. Kinetic expressions for the rate of decomposition of these two tars over the three chars were determined explicitly accounting for the char deactivation with time. The main conclusions extracted from the experimental results are the following:

- In spite of the very different internal structure of the three chars employed, the initial conversion rate (without deactivation) of both tars, toluene and naphthalene, over the three chars and its evolution with time was of the same order.

- The initial activity to decompose naphthalene (the lightest PAH of the two tars tested) of coconut char is similar to that of commercial biomass char (this latter estimated from literature data), both these chars being slightly more active than DSS and coal char.

- Naphthalene is decomposed slightly faster than toluene at temperatures up to 850°C regardless of the char used but the difference is negligible at 950°C. The two tar compounds can be completely converted over the three fresh chars for gas residence time of 0.3 s and temperature above 850°C. At 950°C, the gas residence time needed for complete conversion was 0.2 s.

- The tar conversion over char is catalyzed by certain active sites present in the char matrix. The mechanism of conversion is explained by the tar dehydrogenation with coke formation over the carbonaceous surface and simultaneous gasification of the soot. Thus, gasification of soot is seen as the mechanism to recycle the sites for further tar reaction, maintaining the char activity or, at least, retarding its deactivation.

- The initial tar conversion can be maintained with time if the carbon consumption rate by gasification is higher than the carbon deposition rate. Temperature of 950°C and steam concentration of 15% virtually prevent the deactivation of the three chars.

- The simulation of the FLETGAS gasifier using the DSS kinetics has confirmed that the naphthalene in the gas can be reduced effectively over a moving bed of DSS char (third stage of FLETGAS gasifier). It has been shown that steam and temperature have to be kept high enough in the moving bed to maintain the activity of the char. It was found during the simulation of the pilot plant (to be constructed) that the char is deactivated along the bed, dropping its activity about 40% in 0.5 m for the tested conditions (see Section 3.4.3). Nevertheless, since the naphthalene is the less reactive PAH tar in the gas mixture, the gas produced from the FLETGAS gasifier is expected to fit the requirements for the use in an engine.

CHAPTER 6

Conclusions

Gasification in fluidized bed for power production in small to medium scale plants is an interesting alternative for biomass and waste valorization. However, the presence of heavy organic compounds (tars) in the product gas and the low carbon conversion achieved limit the commercial development of this technology. To overcome these inherent limitations of conventional fluidized bed gasifiers a novel three stage system (FLETGAS) is under development at the Bioenergy Group (University of Seville).

Additional works have been published during the development of the FLETGAS project (Gomez-Barea et al., 2010b; Gómez-Barea et al., 2012; Gómez-Barea et al., 2013; Nilsson et al., 2012a). In another thesis a model of the three stage gasifier was developed (Nilsson, 2012). The main achievements of that thesis work were 1- the characterization of the fluid dynamics of the system, 2- the study of devolatilization and char gasification rates for different waste fuels and 3- the simulation and optimization of the operating conditions of the three–stage system.

The present thesis complements the results obtained in (Nilsson, 2012) to better understand the various steps in the FLETGAS process. Two main tasks are developed in the present thesis. The first task aims at studying the influence of operational variables on tar formation and its homogeneous conversion. The particular objectives of this task are to clarify the homogeneous conversion mechanisms of tars and light hydrocarbons and to determine the experimental conditions reducing the proportion of heavy tars in the product gas. The results are intended to understand conversion processes involving tars and light hydrocarbons in the range of temperature 600–900°C. The processes of formation/generation of volatiles released from the fuel particle and the secondary conversion of these volatiles at different temperatures are investigated separately. This information is useful to establish the operating conditions in the various zones of the FLETGAS gasifier.

The second task included in the present work deals with the study of the conversion of aromatic tars over different carbonaceous materials (chars). This study aims at

obtaining a kinetic expression for tar conversion accounting for char deactivation with time. The kinetics are used for the design of the moving bed (third stage) of the FLETGAS gasifier.

To achieve these objectives two experimental plants were designed and constructed. The devolatilization tests were carried out in a laboratory fluidized bed reactor, whereas the tar conversion over char tests were conducted in a laboratory fixed bed reactor.

This chapter summarizes the main conclusions extracted from the experimental work and identifies the main aspects that need further research.

1. Summary of contributions

The main contributions from this thesis are summarized below, ordered by apparition in the chapters.

Optimization of tar in an autothermal FBG for wastes/biomass at medium scale: identification of measures to be applied in new gasifier developments (Chapter 1).

Measures to optimize fuel conversion in order to achieve high tar conversion in FBG for biomass and waste have been studied over the last three decades. The treatment of tarry gas downstream of the gasifier is complex and expensive for power production in small and medium size gasification plants, so methods to improve tar conversion within the gasifier (primary methods) are preferred for such plants. The existing methods for optimization of conventional FBG by primary methods, despite improving the process, have been shown to be insufficient to attain the gas purity required for burning the gas in an engine to produce electricity (see the list below). Staged gasification creates zones in the gasifier, which promote high conversion of char and tar, and therefore, it is an effective way to conduct gasification. Various developments for small-scale gasification have been proposed over the last decade based on fixed or moving bed, but none of them has still reached commercial status. A new three-stage gasifier (FLETGAS) is under development taking into account the lessons learned during the last decades from the measures taken in conventional gasifiers to minimize the tar concentration in the gas. The main considerations are listed in the following:

1. Increasing the temperature of the gasifier enhances thermal cracking and reforming of tars. In an autothermal FBG the temperature is increased by raising the oxygen to fuel ratio, but the increment of oxygen further burns the light gases, which reduces the process efficiency. In the range of temperature achievable in conventional FBG (800-900°C) the tar compounds are only partially converted in the reactor, and the share of heavy polyaromatic tars is increased.

2. Measures for tar reduction, such as stratification of the gasification agent by secondary injection or increasing the residence time of tar in the reactor by feeding the fuel at the bottom, reduce the total amount of tar in the gas but lead

to more stable and heavy (polyaromatic) tar compounds in the gas, which increases the dew point of the produced gas.

3. Addition of cheap, solid, catalysts (based on mineral rocks) and steam significantly enhances tar reforming, which reduces the tar concentration in the gas, but these measures are still not sufficient for the gas quality required for power application. Other catalysts, such as those based on nickel, are more efficient for tar reforming but, besides the high cost, they deactivate rapidly in the bed and contaminate the ash, so they are not adequate as a material to be added to the bed.

4. The contact of steam and oxygen with char and with freshly generated tar could effectively reduce the tar. However, this is not possible in conventional FBG due to the lack of contact time caused by bypassing of gas through bubbles and the low proportion of char in the bed.

In the last section, the way in which these lessons are combined with the new data obtained in the present thesis (which are summarized below) are discussed to establish the conditions under which the FLETGAS system should operate.

Influence of temperature (uniform) and steam on FB devolatilization products (Chapter 3)

These tests were made in a laboratory FB with uniform temperature along the whole reactor, i.e. the same temperature in the dense bed and in the freeboard, ranging from 600 to 900°C. Two steam concentrations were used: 0 (only nitrogen) and 30 vol% to study the effect of steam. The influence of both variables on light hydrocarbons composition and the yields of tars (gravimetric tar and aromatic tar classes (see section 2.3.2 in Chapter 3)) was studied. The main conclusions obtained are presented in the following:

5. Steam does not significantly influence the yields of aromatic tar and light hydrocarbon compounds at the range of temperature tested. A slight decrease in the yield of gravimetric tar (which includes both aromatic and non-aromatic tars) has been found. Due to the negligible variation of aromatic compounds with steam, it is suggested that steam only promotes the conversion of the non-aromatic tar fraction under the operating conditions tested.

6. The results from the elemental analysis of gravimetric tars demonstrate that even at high temperature (900°C) the presence of heteroatomic (O, N and S) compounds is significant in the condensable fraction. The amounts of thiophene and benzonitrile measured by GC-MS confirmed the high stability of these compounds even at high temperatures. This finding is of relevance when using fuels with a high content in N or S, such as DSS, since the final tar composition could contain high proportion of these compounds.

7. The gravimetric tar, even at the highest temperature tested (900°C), doubled the yield of aromatic tars measured by GC-MS. This indicates that the tar mixture in the gas contains a significant fraction of undetectable (by GC-MS) tar compounds (Tar class 1, see Table 2.2). Since the GC-MS tars are commonly used to estimate

the tar dew point, the high proportions of undetectable tars (that could be composed of heavy compounds condensing at high temperature) implies that these dew point estimations using the tar composition obtained by GC-MS is questionable, i.e. most probably the temperature at which the dew is formed will be higher than that calculated by standard procedure (dew point method from GC-MS analysis).

8. The saturated hydrocarbons (C3 and C_2H_6) and alkyl-aromatic tars increased markedly as the temperature was raised from 600°C to 700°C, decreasing at higher temperature (700-900°C) due to dehydrogenation and C-C bond scission reactions. The yields of CH_4, C_2H_2 and aromatic tars increased with temperature in the whole range of temperature studied (600-900°C).

9. The correlations obtained between tar and light hydrocarbon compounds (methane-benzene, methane-tar class 4 and acetylene-tar class 5) can be used as a shortcut method for the estimation of the yield of heavy tars and aromaticity of the mixture from light hydrocarbon measurements. Besides, the analysis of the observed relations provides an understanding of the mechanisms of tar conversion into light hydrocarbon species during devolatilization in FB.

Influence of temperatures of dense bed and freeboard of an FB on the generation and secondary conversion on volatiles (Chapter 4)

These tests were also made in the laboratory FB reactor. However in this chapter the temperatures in the dense bed and in the freeboard were independently adjusted between 500 and 800°C to specifically study the influence of generation and secondary conversion on the volatile yields. It was also studied the influence of the dried sewage sludge (DSS) particle size between 1 and 5 mm and the differences between the volatiles composition of DSS and wood. The main conclusions obtained are:

10. The increase in the dense bed temperature from 500°C to 800°C enhanced the production of light gas compounds (carbon oxides, hydrogen and light hydrocarbons) while the influence on tar yields is less pronounced.

11. The yield of gravimetric tar was insensitive to the dense bed temperature between 500°C and 700°C, but it decreased 30 wt% when temperature was raised from 700°C to 800°C.

12. The yields of Tar class 4 and 5 (light and heavy polyaromatic hydrocarbons) were hardly affected by the dense bed temperature in the range of 500 to 800°C provided that the contact time between the primary volatiles and the dense bed is short enough to prevent the tar polymerization reactions yielding PAH. This conclusion could be of general application for fuel particles that keep floating during most of the devolatilization time, as the DSS granulates investigated in the present work.

13. The DSS particle size (from 1 mm up to 5 mm) did not affect the tar composition in tests with uniform temperature in the reactor of 800°C.

14. The increase of freeboard temperature from 600 to 800°C strongly enhanced the secondary conversion of volatiles, producing light gas and PAH due to the decomposition of primary tars.

15. For a given freeboard temperature (higher than that in the dense bed) the fate of tars was mainly defined by the freeboard temperature, being rather insensitive to the dense bed temperature.

16. DSS produces more tar (gravimetric and total CG-MS) than wood during devolatilization but the production of PAH (Tar class 4 and 5) was similar for both fuels. Furthermore the trends in the tar yields with the variation of the dense bed and the freeboard temperatures were similar for both fuels, suggesting that similar conversion mechanisms occur during the conversion process, regardless of the parent fuel.

17. The operating conditions in the FB reactor affect the relations between the yields of light hydrocarbons and tars (Contribution 9). Then, they should be used carefully within the experimental conditions for which they have been derived.

Tar conversion over char (Chapter 5)

The tests of tar conversion over char were made in the fixed bed reactor. The different char materials were placed inside the reactor and model tars (toluene and naphthalene) were doped to the carrier gas. The influence of the temperature (between 750 and 950°C), steam concentration in the gas (from 0 to 25 vol%) and internal structure of the char on the tar conversion rate was studied. The main conclusions obtained are:

18. The initial conversion rate (without deactivation) of aromatic tars over the different chars studied and its evolution with time (test duration) was of the same order in spite of their different internal structures. This fact implies that the internal structure of the char has not a direct relation with its activity.

19. The initial activity of coconut char to decompose naphthalene (the lightest PAH of the two used) is similar to that of commercial biomass char (this latter estimated from literature data), both these chars being slightly more active than DSS and coal char.

20. Naphthalene is decomposed slightly faster than toluene at temperatures up to 850°C regardless of the char used but the difference is negligible at 950°C. The two tar compounds can be completely converted over the fresh chars for gas residence time in the char bed of 0.3 s and temperature above 850°C. At 950°C, the gas residence time needed for complete conversion was 0.2 s.

21. The tar conversion over char was found to be catalyzed by certain active sites present in the char matrix. The mechanism of conversion follows a sequence of tar deposition as soot in the char surface and a further gasification of the soot deposited.

22. The initial tar conversions can be maintained with time if the carbon consumption rate by gasification is higher than the carbon deposition rate. A temperature of 950°C and a steam concentration of 15% virtually prevent the deactivation of the chars.

23. The simulation of the FLETGAS gasifier using the DSS kinetics has shown that the naphthalene in the gas can be reduced effectively over a moving bed of DSS char (third stage of the FLETGAS gasifier). It has been shown that the steam concentration and the temperature have to be kept high enough in the moving bed to maintain the activity of the char. It was found during simulation of the pilot plant to be constructed (14 kg/h of incoming DSS char and moving bed of 0.3 m internal diameter) that the char is deactivated along the bed, dropping its activity about 40% in 0.5 m. Since the naphthalene is the less reactive PAH tar in the gas mixture, the gas produced from the FLETGAS gasifier is expected to fit the requirements for the use in an engine.

2. Application of the results obtained on tar conversion to establish operating conditions in the new FLETGAS gasifier

Based on the main results summarized above, recommendations are given in the following to identify guidelines for the operating conditions in the FLETGAS gasifier enabling the production of a gas with low enough dew point.

The first step (FB devolatilization) should be set within the lower range of temperature of autothermal stand-alone FBG (700-750°C). At this temperature the product gas contains a high proportion of primary and secondary tars (see Table 2.2) and low content in light gases (including light hydrocarbons). There is no reason to feed steam in the first stage since at this low temperature the char is not significantly gasified and the effect of steam on tar composition is limited (Contribution 5). The use of enriched air could be interesting since the gas produced is less diluted with nitrogen. However, the use of enriched air lowers the total flowrate of fluidizing agent for a given O_2 to fuel ratio, affecting the fluid-dynamics of the reactor for a given throughput (fuel flowrate divided by the cross section of the bed). This has to be taken into account when selecting the bed material properties (density and diameter) and when the gasifier has to process fuels with different physical properties.

By increasing the oxygen flowrate to the first step of the gasifier, higher temperatures (800-850°C) could be achieved for a given throughput, increasing the yield of volatiles and reducing the char yield. However higher temperatures produce higher yields of PAH (Contribution 14) that cannot be reformed even at 1100°C (Jess, 1996). To prevent the formation of heavy PAH (Contribution 12) a reasonable choice is to feed the steam necessary for the third stage (moving bed of char) just above the dense bed. This measure rapidly cools down the gas produced preventing the tar polymerization reactions.

The tar conversion in the second stage (high temperature reformer) has not been studied in the present thesis. However it is known that 1- aromatic tars are hardly reformed even at high temperatures (Jess, 1996) and 2- non-aromatic tars (primary and secondary) are more reactive and their yields are reduced in the presence of steam (Contribution 5). Hence, it is expected that the steam reforming at high temperature converts effectively the non-aromatic tars from the first stage. This is still not well understood and there are contradictory results in literature. In any case, the high temperature achieved in this stage is expected to produce PAH even in the presence of steam (Brandt et al., 2000). The main role of this second stage is to increase the gas temperature to maintain active the char in the third stage for tar reduction and to provide the necessary steam to convert the char (and soot) at significant rate along the moving bed (Contributions 22 and 23). Then the steam addition is justified in this stage (if it is not added in the first stage) not only to reform the primary tars but also to improve the performance of the third stage.

In the third stage the main requirement is to select operation conditions maintaining the char activity for tar conversion (Contribution 22) and carbon conversion (Nilsson et al., 2012). These conditions are achieved by adjusting the flowrate of steam in the two previous stages, as stated above. It has been shown that the decrease in the tar concentration is not significant above 0.5 m of char bed for the residence time of the gas simulated (1 s). Char conversion may still be significantly increased from 0.5 m up to 1 m (Nilsson et al., 2012) but there is a significant increase in the bed pressure drop. Therefore, a trade-off must be found for the selection of the char bed length (the diameter is fixed by the residence time of the gas required for the nominal gas flowrate). If the char bed is decided to be kept short enough to maintain the system under moderate pressure, an effective way to increase char conversion is the recirculation of the solids stream from the third to the first stage. However, the activity of the char in cycles of carbon conversion-soot deposition, such as the one that could occur under this mode of operation, should be tested.

3. Limitations of the results and further research

Various aspects of this thesis deserve further investigation. In addition, to fully understand the way in which the results obtained in the present thesis can be used in FB gasifiers, and in particular in the FLETGAS gasifier, the main limitations of the results should be clearly pointed out. These issues are briefly discussed in the following, where works to be made to overcome limitations are outlined.

Scaling of FB devolatilization results

In the present work the influence of various parameters affecting the volatile yields during DSS devolatilization has been studied in a batchwise operated laboratory FB fed with nitrogen-steam mixtures at imposed temperature (by adjusting the external heating) employing a fluidization velocity close to that of minimum fluidization. This way of operation made it possible to conduct the tests in such a controlled way that investigation on the mechanisms of tar conversion and the interaction between

volatiles was possible. Nevertheless, the final aim of the work is to obtain helpful data representative of FB gasifier, to identify the process conditions at which these units should be operated in order to minimize the tar production. Obviously, the conditions in which the fuel particles are devolatilized in such laboratory device are far from those found in the target units, i.e. commercial FB gasifiers. In the latter oxygen is part of the fluidization agent, which contains also other gases (mainly CO, CO_2, H_2, and CH_4). Moreover, there is a continuous feeding of biomass and no external heating is applied. In addition, the fluidization velocity in a commercial unit is several times above the minimum fluidization velocity, inducing higher rates of solid and gas mixing than those in the laboratory FB. How to scale the results has been a matter of long discussions with reviewers during the publication of the papers in which this thesis work are based. Therefore, although the main considerations have already been detailed in different parts of Chapters 2-4, we underline in the following the main hypothesis and facts supporting the scaling up of the results.

- In FBG units the oxygen concentration decays rapidly with the height from injection ports and the particles devolatilize near the bed surface. Then the interaction of volatiles with oxygen is limited to particular zones of the gasifier. This makes the tar conversion process to be mainly driven by the temperature profile of the gasifier, as it has been assumed in the present work. In the case that the fluidization agent containing oxygen is injected also in the freeboard of a FBG (secondary air), the analysis of Chapter 4 is still useful to assess secondary conversion of the tars. In staged gasification such as the FLETGAS gasifier, various thermal levels are created in the gasifier by staging the oxidant: the fuel is devolatilized at relatively low temperature by decreasing the amount of oxygen supplied to the devolatilization zone; the temperature is increased in a second zone by addition of the remaining oxygen. In this case the first step is closer to a devolatilizer than a gasifier. It is concluded that for the purpose of tracking the tar conversion process the approach taken in this work is consistent for the target FBG units.

- The influence of the composition of the fluidizing gas on the distribution of products during devolatilization of DSS particles was found to be small in previous work (Nilsson, 2012). Therefore, the yields obtained using nitrogen can be assumed valid under gasification conditions, where a complex gas mixture surrounds the particle during devolatilization. The reason is that the flow of volatiles out of the particle during devolatilization, prevents the fluidizing gas to penetrate into it.

- Although the tests were conducted at a gas velocity lower than that in commercial FB units, the test results obtained here are still applicable to commercial FB units. On the one hand, in the latter the operation is conducted at a gas velocity several times that of minimum fluidization but the heat transfer coefficient is hardly affected by the gas velocity because the fuel particles are converted in the emulsion where the flow conditions are close to that of minimum fluidization (the gas in excess pass in the form of bubbles). On the other hand, the mixing and uniform temperature in an industrial FB is achieved by using high gas velocity, since the bubbles are the stirring mechanism in the bed. In the tests conducted

here, the uniform temperature is achieved at the low gas velocities by keeping the mass ratio between the fuel and the bed material low and by uniform distribution of the heat flux in the oven.

To confirm the main conclusions from this part of the work, pilot test should be conducted under continuous operation. The modifications necessary for the laboratory FB reactor used in this work to handle continuous operation (with continuous feeding of fuel) is under development.

Kinetics model for fuel devolatilization to predict the tar conversion processes

The information obtained about tar formation and homogeneous conversion of volatiles in Chapter 3 and 4 are being used for the development of a fundamental tar conversion model in homogeneous phase. This will be useful for the simulations of the tar mixture composition in FBG under different conditions. In particular, the kinetic model will be implemented in the existing FLETGAS model, where this level of detail was neglected during simulation of the first and second stages (Nilsson, 2012) due to the uncertainty of the models and kinetics developed for biomass and wastes up to date. Furthermore, other thermochemical processes such as FB boilers can benefit from a devolatilization model such as the one to be developed from the data of this thesis work.

Further research on tar conversion over char bed

During the study of the tar conversion over char beds it was demonstrated that the internal structure of the char did not significantly affect its activity. Further research is necessary to determine 1- the influence of the thermal history of the char used on the tar conversion rate, i.e. the influence of producing the char in-situ; 2- the origin of the proposed “active sites” where the tars are converted and 3- the influence of the initial conversion of the char particles since the loop-seal of the FLETGAS gasifier can be designed to partially convert the char fed to the third stage. A kinetic model based on more fundamental steps is under development for the tar conversion over char. Additional tests are being conducted to investigate the main steps of the mechanism identified in this thesis.

Study of tar conversion in the second stage of the FLETGAS gasifier

The study of the tar conversion by oxidation/reforming at temperatures in the range 1000−1200°C is necessary to understand the effects of operating conditions over the composition of the tar mixture produced in the second stage and the mechanisms involved during its transformation. The main operating conditions to be studied are the amount of oxygen and steam fed to the process and the composition of the input tar mixture. Due to the complexity of feeding a gas with the composition of a low−temperature FBG (such as that produced in the first stage of the FLETGAS), this study shall be conducted once the FLETGAS pilot plant is constructed. Therefore, the results are expected to be useful for the redesign of the second stage.

Nomenclature

a	kinetic activity (-)
C_{tar}	tar concentration (mol/m^3)
E_a	activation energy (kJ/mol)
k	rate coefficient (s^{-1})
k_0	frequency factor (s^{-1})
k_d	parameter of the empirical equation given in Eq. 5.6 (min^{-p})
p_1 and p_2	parameters of the empirical equation given in Eq. 5.7 (-)
$-r_{tar}$	tar decomposition rate over char bed (mol/m^{3}s)
t_{ex}	test time (min)
τ	residence time of the gas in the char (s)
Y	yield of different species given by the correlations in Fig. 3.8 and 3.11 (mg/g DSS daf)
χ	tar conversion (-)

Abbreviations

AAEM	alkali and alkaline-earth metallic species
ANVT	aromatic non-volatile tars
daf	dry and ash free fuel
DSS	dried sewage sludge
FBG	fluidized bed gasification/gasifier
FB	fluidized bed
GC–MS	gas chromatography – mass spectrometry
HACA	hydrogen abstraction carbon addition
PAH	poly-aromatic hydrocarbons
TLH	total light hydrocarbons

References

Abu el-Rub, Z.; Bramer, E.A.; Brem, G.; Review of catalysts for tar elimination in biomass gasification processes. Ind. Eng. Chem. Res., 2004; 43, 6911.

Abu el-Rub, Z.; Bramer, E.A.; Brem, G. Experimental comparison of biomass chars with other catalysts for tar reduction. Fuel, 2008; 87, 2243.

Adegoroye, A.; Paterson, N.; Li, X.; Morgan, T; Herod, A.A.; Dugwell, D.R.; Kandiyoti, R. The characterization of tars produced during the gasification of sewage sludge in a spouted bed reactor. Fuel, 2004; 83, 1949.

Aguado, R.; Olazar, M.; San José, M.J.; Aguirre, G.; Bilbao, J. Pyrolysis of sawdust in a conical spouted bed reactor. Yields and product composition. Ind. Eng. Chem. Res., 2000; 39, 1925.

Aznar, M.; Manyá, J.J.; García, G.; Sánchez, J.L.; Murillo, M.B. Influence of freeboard temperature, fluidization velocity, and particle size on tar production and composition during the air gasification of sewage sludge. Energy and Fuels, 2008; 22, 2840.

Bayarsaikhan, B.; Sonoyama, N.; Hosokai, S.; Shimada, T.; Hayashi, J.I.; Li, C.Z. ; Chiba, T. Inhibition of steam gasification of char by volatiles in fluidized bed under continuous feeding of a brown coal. Fuel, 2006; 8, 340.

Brage, C.; Yu, Q.; Sjöström, K. Characteristics of evolution of tar from wood pyrolysis in a fixed-bed reactor. Fuel 1996; 75, 213.

Brandt, P.; Larsen, E.; Henriksen, U. High tar reduction in a two-stage gasifier. Energy & Fuels, 2000; 14, 816.

Bruinsma, O.S.L.; Moulijn, J.A. The pyrolytic formation of polycyclic aromatic hydrocarbons from benzene, toluene, ethylbenzene, styrene, phenylacetylene and n-decane in relation to fossil fuels utilization. Fuel Proc. Tech., 1988; 18, 213.

Bruinsma, O.S.L.; Tromp, P.J.J.; de SauvageNolting, H.J.J.; Moulijn J.A. Gas phase pyrolysis of coal-related aromatic compounds in a coiled tube flow reactor. 2. Heterocyclic compounds, their benzo and dibenzo derivatives. Fuel, 1988; 67, 334.

Bui, T.; Loof, R.; Bhattacharya, S.C. Multi-stage reactor for thermal gasification of wood. Energy, 1994; 19, 397.

Campoy M., Gómez-Barea A., Villanueva A.L., Ollero P. Air-steam gasification of biomass in a fluidized bed under simulated autothermal and adiabatic conditions, Ind. & Eng. Chem. Res., 2008; 47, 5957.

Campoy M., Gómez-Barea A., Villanueva A.L., Ollero P. Air-steam gasification of biomass in a fluidized bed: process optimization by enriched air. Fuel Process. Technol., 2009; 90, 677.

Campoy, M.; Gómez-Barea, A.; Fuentes-Cano, D.; Ollero, P. Tar reduction by primary measures in an autothermal air-blown fluidized bed biomass gasifier. Ind. & Eng. Chem. Res., 2010; 49, 294.

Chen, H.; Namioka, T.; Yoshikawa, K. Characteristics of tar, NO_x precursors and their absorption performance with different scrubbing solvents during the pyrolysis of sewage sludge. Applied Energy, 2011; 88, 5032.

Chen, L.; Dupont, C.; Salvador, S.; Boissonnet, G.; Schweich, D. Influence of particle size, reactor temperature and gas phase reactions on fast pyrolysis of beech wood. Int. Jour. of Chem. Reac. Eng., 2010; 8, Article A10.

CEN/TS 15439. Biomass gasification – Tar and particles in product gas – Technical specification, 2006.

Cypres, R. Aromatic hydrocarbons formation during coal pyrolysis. Fuel Proc. Tech., 1987; 15, 1.

den Uil, H. CASST: a new and advanced process for biomass gasification. In: Developments in Thermochemical Biomass Conversion, 17-22 Sept. 00, Tyrol, Austria.

Devi, L.; Ptasinski, K.J.; Jansen, F.J.J.G. A review of the primary measures for tar elimination in biomass gasification processes. Biomass & Bioenergy, 2003; 24, 125.

Dufour, A.; Masson, E.; Girods, P.; Rougaume, Y.; Zoulalian, A. Evolution of aromatic tar composition in relation to methane and ethylene from biomass pyrolysis-gasification. Energy and Fuels, 2011; 25, 4182.

Evans, R.J.; Milne, T.A. Molecular characterization of the pyrolysis of biomass. 1. Fundamentals. Energy & Fuels, 1987; 1, 123.

Fagbemi, L.; Khezami, L.; Capart, R. Pyrolysis products from different biomasses: application to the thermal cracking of tar. Applied Energy, 2001; 69, 293.

Fonts, I.; Gea, G.; Azuara, M.; Ábrego, J.; Arauzo, J. Sewage sludge pyrolysis for liquid production: a review. Ren. and Sust. Ener. Rev. 2012; 16, 2781.

Fuentes-Cano, D.; Gómez-Barea, A.; Nilsson, S.; Ollero, P. The influence of temperature and steam on the yields of tar and light hydrocarbon compounds during devolatilization of dried sewage sludge in fluidized bed. Fuel, accepted.

Gaston, K.R.; Jarvis, M.W.; Pepiot, P.; Smith, K.M.; Frederick, W.J.; Nimlos, M.R. Biomass pyrolysis and gasification of varying particle sizes in a fluidized-bed reactor. Energy & Fuels, 2011; 25, 3747.

Glicksman, L.R.; Hyre, M.R.; Farrell P.A. Dynamic similarity in fluidization. Int. J. Multiphase Flow 20, Suppl., 1994; 331

Gómez-Barea, A.; Vicente-Enamorado, J.M.; Cruz, J.L.; Rodríguez, P.; Campoy, M.; Ollero, P. Commissioning of a 3 MWth demostration unit for biomass gasification in fluidised bed. Proc. 16th European Biomass Conference, Valencia, 2008; 2333.

Gómez-Barea, A.; Leckner, B. Gasification of biomass and waste. In: Strunk Jr. W., White E.B., editors. Handbook of combustion, Wiley-vch; 2009, Vol. 4.

Gómez-Barea, A.; Leckner, B. Modeling of biomass gasification in fluidized bed. Prog. Energ. Combust. Science, 2010; 36, 444.

Gómez-Barea, A.; Nilsson, S.; Barrero, F.V.; Campoy, M. Devolatilization of wood and wastes in fluidized bed. Fuel Proc. Tech., 2010a; 91, 1624.

Gómez-Barea, A.; Fuentes, D.; Nilsson, S.; Tirado, J.; Ollero, P. Fluid-dynamics of a cold model of a fluidized bed gasification system with reduced tar content. Proc 18th European Biomass Conference, Lyon (France), Paper VP2.1.13, 2010b.

Gómez-Barea, A.; Leckner, B.; Villanueva-Perales, A.; Nilsson, S.; Fuentes-Cano, D. Improving the performance of fluidized bed biomass/waste gasifiers for distributed electricity: A new three-stage gasification system. Appl. Ther. Eng., 2012; 50, 1453.

Gómez-Barea, A.; Ollero, P.; Leckner, B**.** Optimization of char and tar conversion in fluidized bed biomass gasifiers. Fuel, 2013; 103, 42.

Griffiths, D.M.L.; Mainhood, J.S.R. Cracking of tar vapor and aromatic compounds on activated carbon. Fuel, 1967; 46, 167.

Hamel, S.; Hasselbach, H.; Weil, S.; Krumm, W.. Autothermal two-stage gasification of low-density waste-derived fuels. Energy, 2007; 32, 95.

Han, J.; Kim, H.; The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renew. Sust. Energ. Rev., 2008; 12, 397.

Hayashi, J.I.; Kawakami, T.; Taniguchi, T.; Kusakabe, K.; Morooka, S. Control of molecular composition of tar by secondary reaction in fluidized-bed pyrolysis of a subbituminous coal. Energy & Fuels, 1993; 7, 57.

Hayashi, J.I.; Nakagawa, K.; Kusakabe, K.; Morooka, S.; Yumura, M. Change in molecular structure of flash pyrolysis tar by secondary reaction in a fluidized bed reactor. Fuel Proc. Tech., 1992; 30, 237.

Hayashi, J.I.; Takahashi, H.; Iwatsuki, M.; Essaki, K.; Tsutsumi, A.; Chiba, T. Rapid conversion of tar and char from pyrolysis of a brown coal byreactions with steam in a drop-tube reactor. Fuel, 2000; 79, 439.

Hayashi, J.I.; Iwatsuki, M.; Morishita, K.; Tsutsumi, A.; Li, C.Z.; Chiba, T. Roles of inherent metallic species in secondary reactions of tar and char during rapid pyrolysis of brown coals in a drop-tube reactor. Fuel, 2002; 81, 1977.

Henriksen, U.; Ahrenfeldt, J.; Jensen, T.K. ; Gobel, B.; Bentzen, J.D. ; Hindsgaul, C.; Sorensen, L.H. The design, construction and operation of a 75 kW two-stage gasifier, Energy, 2006; 31, 1542.

Higman, C.; van der Burgt, M. Gasification, 2nd ed., Gulf Professional Publishers/Elsevier Science, Amsterdam, 2008.

Horne, P.A.; Williams, P.T. Influence of temperature on the products from the flash pyrolysis of biomass. Fuel, 1996; 75, 1051.

Hosokai, S.; Hayashi, J.I. ; Shimada, T.; Kobayashi, Y.; Kuramoto, K.; Li, C.Z. ; Chiba, T. Spontaneous generation of tar decomposition promoter in a biomass steam reformer. Chem. Eng. Res. Des., 2005; 83, 1093.

Hosokai, S.; Kumabe, K.; Ohshita, M.; Norinaga, K.; Li, C.Z.; Hayashi, J.I. Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity. Fuel, 2008; 87, 2914.

Hosokai, S., Norinaga, K., Kimura, T., Nakano, M., Li, C.Z., Hayashi, J.I., Reforming of volátiles from the biomass pyrolysis over charcoal in a sequence of coke deposition and steam gasification of coke. Energy & Fuels, 2011; 25, 5387.

Houben, M.P. Analysis of tar removal in a partial oxidation burner. PhD thesis, 2004.

Houmoller, S.; Hansen, M.W.; Henriksen, U. Two-stage fluid bed pyrolysis and gasification unit. Proceedings of Biomass for Energy and Industry 9th European Conference and Technology Exhibition 24-27 June 1996, Copenhagen, Denmark.

Ito, K.; Moritomi, H.; Yoshiie, R.; Uemiya, S.; Nishimura, M.; Tar capture effect of porous particles for biomass fuel under pyrolysis conditions. Chem, J. Eng. Jpn., 2003; 36, 840.

Jess, A. Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels. Fuel, 1996; 75, 1441.

Jönsson, O. Thermal cracking of tars and hydrocarbons by addition of steam and oxygen in the cracking zone. Fundamentals of Thermochemical Biomass Conversion. Elsevier applied science, 1985; 733.

Juneja, A.; Mani, S.; Kastner, J. Catalytic cracking of tar using biochar as a catalyst, American Society of Agricultural and Biological Engineers Annual International Meeting, Paper number: 1009863; 2010.

Kersten, S.R.A.; Wang, X.; Prins, W.; van Swaaij W.P.M. Biomass pyrolysis in a fluidized bed reactor. Part 1: literature review and model simulations. Ind. Eng. Chem. Res., 2005; 44, 8773.

Kiel, J.H.A. Primary measures to reduce tar formation in fluidized bed biomass gasifiers. ECN-C--04-014, 2004.

Kiel, J.H.A.; van Paasen, S.V.B.; Neeft, J.P.A.; Devi, L.; Ptasinski, K.J.; Janssen, F.J.J.G. Primary measures to reduce tar formation in fluidized-bed biomass gasifiers, Report ECN-C--04-014, The Netherlands, 2004.

Kuramoto, K.; Matsuoka, K.; Murakami, T.; Takagi, H.; Nanba, T.; Suzuki, Y.; Hosokai, S.; Hayashi, J.I. Cracking and coking behaviours of nascent volatiles derived from flash pyrolysis of woody biomass over mesoporous fluidized-bed material. Ind. Eng. Chem. Res., 2009; 48, 2851.

Kurkela, E.; Nieminen, M.; Simell, P. Development and commercialization of biomass and waste gasification technologies for reliable and robust co-firing plants towards synthesis gas production and advanced power cycles. 2nd World biomass conference, Rome, Italy, May 10-14, 2004; Paper PA1.4.

Ledesma, E.B.; Kalish, M.A.; Nelson, P.F.; Wornat, M.J.; Mackie, J.C. Formation and fate of PAH during the pyrolysis and fuel-rich combustion of coal primary tar.Fuel 2000; 79, 1801.

Ledesma, E.B.; Marsh, N.D.; Sandrowitz, A.; Wornat, M.J. Global kinetic rate parameters for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of catechol, a model compound representative of solid fuel moieties. Energy & Fuels, 2002a; 16, 1331.

Ledesma, E.B.; Marsh, N.D.; Sandrowitz, A.K.; Wornat, M.J. An experimental study on the thermal decomposition of catechol. Proceedings of the Combustion Institute, 2002b; 29, 2299.

Lettner, F.; Haselbacher, P.; Timmerer, H.; Leitner, P.; Suyitno, Rasch, B. Latests results of CLEASTGAS-Clean staged biomass gasification CHP. 15th European Biomass Conference & Exhibition, Berlin, Germany, 2007.

Li, C.Z.; Nelson, P.F. Fate of aromatic ring systems during thermal cracking of tars in a fluidized-bed reactor. Energy and Fuels, 1996; 10, 1083.

Lu, M.; Mulholland, J.A. PAH Growth from the pyrolysis of CPD, indene and naphthalene mixture. Chemosphere, 2004; 55, 605.

Manyá, J.J.; Sánchez, J.L.; Gonzalo, A.; Arauzo, J. Air gasification of dried sewage sludge in a fluidized bed: Effect of the operating conditions and in-bed use of alumina. Energy & Fuels, 2005; 19, 629.

Manyá, J.J.; Sánchez, J.L.; Ábrego, J.; Gonzalo, A.; Arauzo, J. Influence of gas residence time and air ratio on the air gasification of dried sewage sludge in a bubbling fluidised bed. Fuel, 2006; 85, 2027.

Marsh, N.; Ledesma, E.B.; Sandrowitz, A.K., Wornat, M.J. Yields of polycyclic aromatic hydrocarbons from the pyrolysis of catechol (ortho-dihydroxybenzene): temperature and residence time effects. Energy & Fuels, 2004; 18, 209.

Matsuhara, T.; Hosokai, S.; Norinaga, K.; Matsuoka, K.; Li, C.Z.; Hayashi, J.I. In-situ reforming of tar from the rapid pyrolysis of a Brown coal over char. Energy & Fuels, 2010; 24, 76.

Matsuoka, K., Shinbori, Kuramoto, K., Nanba, T., Morita, A., Hatano, H., Suzuki, Y. Mechanism of woody biomass pyrolysis and gasification in a fluidized bed of porous alumina particles. Energy & Fuels, 2006; 20, 1315.

McGrath, T.; Sharma, R.; Hajaligol, M. An experimental investigation of polycyclic-aromatic hydrocarbons (PAH) from pyrolysis of biomass materials. Fuel, 2001; 80, 1787.

Milne, T.A.; Evans, R.J.; Abatzouglou, N. Biomass gasifiers “tars”: their nature, formation and conversion, 1998. NREL/TP-570-25357.

Miura, K.; Kawase, M.; Nakagawa, H.; Ashida, R.; Nakai, T.; Ishikawa, T. Conversion of tar in hot coke oven gas by pryolysis and steam reforming. J. Chem. Eng. Jpn., 2003; 36, 735.

Morf, P.O.; Hasler, P.; Nussbaumer, T. Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. Fuel, 2002; 81, 843.

Mun, T.Y.; Kang, B.S.; Kim, J.S. Production of a producer gas with high heating values and less tar from dried sewage sludge through air gasification using a two-stage gasifier and activated carbon. Energy and Fuels, 2009; 23, 3268.

Namioka, T.; Son, Y.; Sato, M.; Yoshikawa, K. Practical method of gravimetric tar analysis that takes into account a thermal cracking reaction scheme. Energy and Fuels, 2009; 23, 6156.

Namioka, T.; Yoshikawa, K.; Hatano, H.; Suzuki, Y. High tar reduction with porous particles for low temperature biomass gasification: effects of porous particles on tar and gas yields during sawdust pyrolysis. J. Chem. Eng. Jpn., 2003; 36, 1440.

Narváez, I.; Orío, A.; Aznar, M.P.; Corella, J. Biomass gasification with air in an atmospheric bubbling fuidized bed. Effect of six operational variables on the quality of produced raw gas. Ind. Eng. Chem. Res., 1996; 35, 2110.

Nelson, P.F.; Smith, I.W.; Tyler, R.J.; Mackie, J.C. Pyrolysis of coal at high temperatures. Energy and Fuels, 1988; 2, 391.

Neves, D.; Thunman, H.; Matos, A.; Tarelho, L.; Gómez-Barea, A. Characterization and prediction of biomass pyrolysis products. Prog. Ener. Combust. Science, 2011; 37, 611.

Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D.; Ollero P. Gasification of biomass and waste in a staged fluidized bed gasifier: Modeling and comparison with one-stage units. Fuel, 2012a; 97, 730.

Nilsson, S.; Gómez-Barea, A.; Fuentes-Cano, D. Gasification reactivity of char from dried sewage sludge in a fluidized bed. Fuel, 2012b; 92, 346.

Nilsson, S.; Modeling and simulation of a three-stage gasification technology for waste and biomass. PhD thesis, 2012.

Paisley, M.A.; Overend, R.P. The Sylva Gas process from future energy resources - a commercialization success, in: W. Palz, J. Spitzer, K. Maniatis, K. Kwant, P. Helm, A. Grassi, (Eds.), Proc 12th European Conference on Biomass for Energy, Industry and Climate Protection, Amsterdam 2002; 975.

Pan, Y.G.; Roca, X.; Velo, E.; Puigjaner, L. Removal of tar by secondary air in a fluidised bed gasification of residual biomass and coal. Fuel, 1999; 78, 1703.

Petersen, I.; Werther, J. Experimental investigation and modeling of gasification of sewage sludge in the circulating fluidized bed. Chem. Eng. Process, 2005a; 44, 717.

Petersen, I.; Werther, J. Three-dimensional modeling of a circulating fluidized bed gasifier for sewage sludge. Chem. Eng. Sci., 2005b; 60, 4469.

Piskorz, J.; Scott, D.S.; Westerberg I.B. Flash pyrolysis of sewage sludge. Ind. Eng. Chem. Process Des. Dev., 1986; 25, 265.

Ponzio A., Kalisz S., Blasiak W. Effect of operating conditions on tar and gas composition in high temperature air/steam gasification (HTAG) of plastic containing waste. Fuel Process. Technol., 2006; 87, 223.

Rabou, L.P.L.M.; Zwart, R.W.R.; Vreugdenhil, B.J.; Bos, L. Tar in biomass producer gas, the Energy research Centre of The Netherlands (ECN) experience: an enduring challenge. Energy & Fuels, 2009; 23, 6189.

Rauch, R.; Hofbauer, H.; Bosch, K.; Siefer, I.; Aichernig, C.; et al., Steam Gasification of Biomass at CHP Plant in Güssing - Status of the Demonstration Plant, Proc. 2nd World Conf on Biomass for Energy, Industry and Climate Protection, Rome, 2004; Vol. II, 1687.

Reichembach de Sousa, L.C. Gasification of wood, urban wastewood (altholz) and other wastes in a fluidized bed reactor. phD thesis, 2001.

Richter, H.; Howard, J.B. Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. Prog. Energ. Combust. Science, 2000; 6, 565.

Safitri, A. Biomass gasification using bubbling fluidized-bed gasifiers: investigation of the effect of different catalyst on tar reduction. PhD thesis, 2005.

Salo, K. Biomass Gasification Plant in Skive. Presented at IV International Seminar of Biomass Gasification. Göteborg. Sweden, 2010.

Sanchez, M.E.; Menéndez, J.A.; Domínguez, A.; Pis, J.J.; Martínez, O.; Calvo, L.F.; Bernad, P.L. Effect of pyrolysis temperature on the composition of the oils obtained from sewage sludge. Biomass and Bioenergy, 2009; 33, 933.

Scheer, A.M.; Mukarate, C.; Robichaud, D.J.; Ellison, B.; Nimlos, M.R. Radical chemistry in the thermal decomposition of anisole and deuterated anisoles: an investigation of aromatic growth. J. Phys. Chem., 2010; 114, 9043.

Scheer, A.M.; Mukarate, C.; Robichaud, D.J.; Nimlos, M.R.; Ellison, B. Thermal Decomposition mechanism of the methoxyphenols: formation of phenol, cyclopentadienone, vinylacetilene and acetylene. J. Phys. Chem., 2011; 115, 13381.

Schmid, C.; Mühlen, H.J. Staged reforming—a thermal conversion process specifically developed for biomass. In: Proceedings of the second Olle Lindström Symposium, 1999; 75.

Sharma, R.K.; Hajaligol, M.R. Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. J. Anal. Appl. Pyrolysis, 2003; 66, 123.

Simell, P. Catalytic Hot Gas Cleaning of Gasification Gas. VTT Publication No 330, 1997.

Souza-Santos, M.L. Solid Fuels Combustion and Gasification, Marcel Dekker, New York, 2004.

Stiles, H.N., Kandiyoti , R. Secondary reactions of flash pyrolysis tars measured in a fluidized bed pyrolysis reactor with some novel design features. Fuel, 1989; 68, 275.

Stevens, D.J. Hot gas conditioning: recent progress with larger-scale biomass gasification systems. NREL, Golden, CO, USA, Report no. NREL/SR-510-29952, 2001.

Sutton, D.; Kelleher, B.; Ross, J.R.H. Review of literature on catalysts for biomass gasification. Fuel Processing Technology, 2001; 73, 155.

Sueyasu, T.; Oike, T.; Mori, A.; Kudo, S.; Norinaga, K.; Hayashi, J.I. Simultaneous steam reforming of tar and steam gasification of char from the pyrolysis of potassium-loaded woody biomass. Energy & Fuels, 2012; 26, 199.

Susanto, H.; Beenackers, A.A.C.M. A moving bed gasifier with internal recycle of pyrolysis gas. Fuel, 1996; 75, 1339.

Taralas, G.; Kontominas, M.G.; Kakatsios, X. Modeling the thermal destruction of toluene (C_7H_8) as tar-related species for fuel gas cleanup. Energy and Fuels, 2003; 17, 329.

Thomas, S.; Ledesma, E.; Wornat, M. The effects of oxygen on the yields of the thermal decomposition products of catechol under pyrolysis and fuel-rich oxidation conditions. Fuel, 2007; 86, 2581.

Timmerer, H.; Haselbacher, P.; Lettner, F.; Rasch, B.; Lankmayr, E.; Ranz, A. Comparison of different analysis methods for organic and inorganic producer gas pollutant with the background of deviant measurements results. Proceedings of the 15th European Biomass Conference and Exhibition, 2007.

Van der Drift, A. An overview of innovative biomass gasification concepts. 12th European Conference and Exhibition on Biomass for Energy and Climate Protection, 17-21 June 2002, Amsterdam.

van der Drift, A.; Carbo, M.C.; van der Meijden, C.M. The TREC-module integration of tar reduction and high-temperature filtration, ECN-RX--05-184, 2005.

van Paasen, S.V.B. Tar formation in a fluidised-bed gasifier. Impact of fuel properties and operating conditions. 2004, ECN-C--04-013.

van Paasen, S.V.B.; Cieplik, M.K.; Phokawat, N.P. Gasification of non-woody biomass. 2006, ECN-C-06--032.

Wang, X.; Kersten, S.R.A.; Prins, W.; van Swaaij, W.P.M. Biomass pyrolysis in a fluidized bed reactor. Part 2: Experimental validation of model results. Ind. Eng. Chem. Res., 2005; 44, 8786.

Wang, Y.; Namioka, T.; Yoshikawa, K. Effects of the reforming reagents and fuel species on tar reforming reaction. Biores. Tech., 2009; 100, 6610.

Wang, Y.; Yoshikawa, K.; Namioka, T.; Hashimoto Y. Performance optimization of two-staged gasification system for woody biomass. Fuel Proc. Tech., 2007; 88, 243.

Werther, J.; Ogada, T. Sewage sludge combustion. Prog. Energ. Combust. Science, 1999; 25, 55.

Williams, P.T.; Taylor, D.T. Aromatization of tyre pyrolysis oil to yield polycyclic aromatic hydrocarbons. Fuel, 1993; 72, 1469.

Wornat, M.; Ledesma, E.B.; Marsh, N.D. Polycyclic aromatic hydrocarbons from the pyrolysis of catechol (ortho-dihydroxybenzene), a model fuel representative of entities in tobacco, coal and lignin. Fuel, 2001; 80, 1711.

Thersites: www.thersites.nl

Xu, W.; Tomita, A. The effects of temperature and residence time on the secondary reactions of volatiles from coal pyrolysis. Fuel Proc. Tech., 1989; 21, 25.

Zhang, Y.; Kajitani, S.; Ashizawa, M.; Oki, Y. Tar destruction and coke formation during rapid pyrolysis and gasification of biomass in a drop-tube furnace. Fuel, 2010; 89, 302.

Appendix i

Development of a procedure for tar sampling and analysis

In this section the procedure for tar sampling and analysis developed in this thesis for the quantification of aromatic tar compounds is presented.

Ai.1- Introduction

To develop a methodology for tar analysis two main facts has to be considered: 1- the nature of the tars in the gas and 2- whether it is necessary the characterization only or the quantification of the tar compounds is also needed. The tar composition, as discussed in Chapter 1, strongly depends on the operating conditions of the process where they are produced. The tar mixture of flash pyrolysis, operated between 450-600°C) is composed of hundreds of individual compounds. The tars produced at this temperature are composed of fragments of the parent fuel structure and contain a high proportion of heteroatoms and aliphatic chains. In contrast, the tar mixture produced in biomass gasification, at temperature between 750-950°C, is less complex and contains only dozens of compounds, most of them comprising polyaromatic hydrocarbons (PAH). Due to the complexity of pyrolysis tars, a detailed quantification of the tar compounds in the mixture is an unaffordable task. Hence most works analyzing pyrolysis tars conduct other (and simpler) analysis such as tar characterization (by mass-spectrometry), quantification of the most relevant compounds or elemental analysis of the tar mixture.

The tar sampling was a difficult issue up to the publication of a standard guide for tar sampling (and analysis) in gasifiers (CEN/TS 15439, 2006). Before the publication of this standard a wide number of tar sampling methods were used by different researches and institutions, making it difficult the comparison of results from one author to another.

This section summarizes the sampling and analysis procedure for tar measurements focusing on the GC-MS analysis protocol developed for aromatic compounds

quantification. The methodology followed for analyzing the tar samples is based on that described in (CEN/TS 15439, 2006). However some modifications, described in the following, were conducted to achieve better results.

Ai.2- Tar sampling; device and procedure

The tar sampling device used during this thesis is based on that described in (CEN/TS 15439, 2006) with some modifications. This standard is based on the capture of the tar compounds in liquid solvents (not based in solid phase adsorption or SPA). SPA has some advantages over the tar capture by solvents such as the lower solvent consumption or the lower time of sampling. The volume of gas sampled in the SPA method is 100 ml (approx.) while the tar capture by solvents needs larger volumes (100-500 l) of gas. During the tests conducted in the present thesis large volumes of gas were sampled making impossible the use of SPA method.

In the experiments conducted in this thesis the gas leaving the reactor was nearly free of particles, so there was no need for installing the modules of gas preconditioning, particle filter and volume metering described in (CEN/TS 15439, 2006). Then only the tar collection module was installed. The design of this module was based on the tar train collector instead on the Petersen column. In the standard configuration (CEN/TS 15439, 2006) three impingers are kept at ambient temperature and two impingers at -20°C, however using this configuration the tar capture was not complete and it was decided to modify the train configuration to improve the tar capture efficiency. The modified tar train comprises seven impingers with 35 mm of internal diameter filled with 50 ml (approx.) of isopropanol immersed in a thermostatic bath at -20°C. The last four impingers had glass frits at the bottom of the discharge tube to improve the gas-solvent contact.

The solvent was recovered after each test and the train was washed with acetone. Both solvents (isopropanol from the impingers and acetone used for washing) were mixed and stored at -20°C during one month maximum before its treatment. The effectiveness of the train developed for tar trapping was checked by conducting dedicated test both for devolatilization tests (tests of Chapters 3 and 4) and tar conversion over char (Chapter 5). By analyzing the liquid of the last impinger, it was only detected traces of light tars in the last impinger during devolatilization tests, and traces of toluene (also negligible amounts) during the tests of tar conversion over char. During the tests themselves, the effectiveness of tar capture was not further determined by analyzing the liquid of the last impinger separately, but only the colorlessness of the liquid in the two last impingers was checked.

Although the tar solutions were almost free of particles they were filtered and further filled to 500 ml with isopropanol at ambient temperature. Two aliquots of 15 ml were taken for GC-MS analysis and the other 470 ml were used for gravimetric determination. The gravimetric tar samples (after distillation) were analyzed to determine their elemental composition. The GC-MS analyses and the elemental analyses of the gravimetric tar were conducted in the CITIUS facilities while the distillations for gravimetric determination were done in the AICIA laboratories.

Ai.3- Tar analyses

Ai.3.1- Gravimetric tar analysis

Vacuum distillation in a rotary evaporator at 1,5 KPa (abs) and 55°C was applied to the tar solution. Once the tar is considered totally evaporated the sample is weighted (at ambient temperature) and re-distilled in the same conditions. The gravimetric distillation was finished when constant weight was achieved.

The gravimetric tar yield was then obtained by the expression:

$$Gravimetric\ yield\left(\frac{mg\ tar}{g\ daf\ \ fuel}\right)=\frac{Gravimetric\ weight\,(mg)\bullet\left(\frac{500\,(ml)}{470\,(ml)}\right)}{Weight\ of\ \ daf\ \ fuel\,(g)} \qquad \text{(Ai-1)}$$

Ai.3.2- Elemental analysis of gravimetric tar

The residue after the gravimetric tar analysis was sent to an external laboratory (CITIUS) for the quantification of carbon, hydrogen, nitrogen and sulfur. The analyses were carried out with an elemental analyzer LECO CHNS 932. The oxygen concentration was determined by difference assuming other elements are not present in the sample.

Ai.3.3- GC-MS analysis

GC-MS analysis for aromatic compounds

With the main objective of determining the concentration of the aromatic tar compounds in the tar mixture, a method based on a chromatographic analysis was developed. The bases of the method for GC-MS analysis are similar to those described in (CEN/TS 15439, 2006), however further details were taken from (Rochembach, 2001). The Gas Chromatography coupled to a Mass Spectrometer detector (GC-MS) enables the characterization of the tar compounds in the mixture and the quantification of these compounds.

The GC-MS device used was an Agilent mod. 6890N (GC) coupled to a Micromass Autospec-Q (MS) equipped with an electronic impact (EI) ionisation source (GC-EI-MS). The GC column used was a 60 m x 0.25 mm i.d., 0.25 µm film thickness TRB-Meta X5 similar to that used in (Rochembach, 2001). The main conditions of the chromatographic analysis were:

- Oven temperature program: from 40°C at 10°C/min to 300°C (26 min) and then the column is maintained at 300°C for 9 min.
- Carrier gas: a constant flow of Helium (1.5 ml/min) was used as carrier gas for all analysis runs.
- Injector temperature and split conditions: the injector temperature was maintained at 250°C. The sample size was 1 µl with a split ratio of 1:20.

Some preliminary analyses were conducted in *Scan* mode, in a range of 30-650 amu, to identify the different aromatic molecules in the samples. According with these analyses, the aromatic compounds present in significant proportion were selected for analysis. Table Ai-1 presents the compounds analysed by GC-MS. The list includes some compounds identified as isomers of other tars. These compounds are presented in Table Ai-1 as "PAH (tar compound isomer)". These compounds were quantified using the calibration line of its isomer, for example: the "PAH (Pyrene isomer)" was quantified using the Pyrene calibration line. Since the intensity of the MS signal is proportional to the molecular weight and the structure of the compound, the error of this procedure is expected to be low; however, due to the absence of standards for these compounds, it was not possible to check the error systematically.

Once chosen the tars to be analysed (see table Ai-1), the most abundant ion for each compound was identified in the mass spectrometer. The intensity of this ion was selected for the quantification of this specific compound in SIM mode (under SIM mode only the signal of the selected ions are recorded).

One solution containing the standards of the selected tars was prepared before each analysis (standards concentrated solution, SCS). From this concentrated solution four different solutions (standards diluted solutions, SDS) were prepared diluting with isopropanol for the calibration of the system. Three dilutions of each sample solution taken in the tests (sample solutions, SS: the solutions containing the tar captured in the tests) were prepared to ensure that the concentration of each compound is within the limits of the calibrating line. The dilutions prepared were, in most cases, between 1/2 (for diluted compounds, mainly heavy PAH) and 1/10 (for concentrated compounds). Quality control solutions (QCS), having known concentrations of the different tar compounds, were also prepared by diluting with isopropanol the SCS solution. These QCS were used as reference material for estimating the global error of the analysis.

Every solution analysed (SDS, SS and QCS) was doped with a known mass of internal standard to reduce the instrumental interferences. The internal standard selected was 1,2,3,4-tetrahydronaphthalene since it fulfils the main requirements to be internal standard in the tar samples and because in has been used successfully in (Rochembach, 2001).

The samples are injected following the sequence: calibration solutions (SDS) – samples (SS) – quality control solutions (QCS). In each analysis run were analysed: four SDS, from six to ten SS and three QCS. In addition each sample was analysed three times to check the repeatability.

The maximum error allowed for each tar compound, calculated as a percentage of deviation between the real concentration in quality control samples and the concentration measured by GC-MS, was 10%.

Table Ai-1. List of tars analyzed by GC-MS. Mol. Mass: molecular mass, B.P.: boiling point, CAS Nr.: number of identification (Chemical Abstracts Service).

Compound	Tar class (van Paasen, 2004)	Formula	Mol. Mass (g/mol)	B.P. (°C)	CAS Nr.
Benzene	-	C_6H_6	78.11	79.9	71-43-2
Tiophene	2	C_4H_4S	84.14	84.0	110-02-1
Toluene	3	C_7H_8	92.14	110.7	108-88-3
m-xylene (*p*-xylene)	3	C_8H_{10}	106.17	138.4 139.2	106-42-3 108-38-3
Styrene	3	C_8H_8	104.15	145.3	1000-42-5
o-xylene	3	C_8H_{10}	106.17	144.5	95-47-6
Phenol	2	C_6H_6O	94.11	181.8	108-95-2
Benzonitrile	2	C_6H_5CN	103.12	191.0	100-47-0
Benzofuran	2	C_8H_6O	118.14	174.1	271-89-6
Indene	3	C_9H_8	116.16	182.7	95-13-6
m-cresol	2	C_7H_7OH	108.14	202.8	108-39-4
Naphthalene	4	$C_{10}H_8$	128.17	218.0	91-20-3
2-methylnaphthalene	4	$C_{11}H_{10}$	142.20	241.1	91-57-6
1-methylnaphthalene	4	$C_{11}H_{10}$	142.2	245.1	90-12-0
Biphenyl	4	$C_{12}H_{10}$	154.21	256.0	92-52-4
2-ethenylnaphthalene	4	$C_{12}H_{10}$	154.21	248.5	827-54-3
Acenaphthylene	4	$C_{12}H_8$	152.19	280.0	208-96-8
Acenaphtene	4	$C_{12}H_{10}$	154.21	279.0	83-32-9
Dibenzofuran	2	$C_{12}H_8O$	168.19	287.1	132-64-9
Fluorene	4	$C_{13}H_{10}$	166.22	294.1	86-73-7
Phenantrene	4	$C_{14}H_{10}$	178.23	340.1	85-01-8
Anthracene	4	$C_{14}H_{10}$	178.23	340.1	120-12-7
4H-cyclopenta[def]phenanthrene	4	C_{15}-H_{10}	190.24	353.0	203-64-5
Fluoranthene	4	$C_{16}H_{10}$	202.26	385.8	206-44-0
PAH (Fluoranthene isomer)	4	-	-	-	-
PAH (Pyrene isomer)	5	-	-	-	-
Pyrene	5	$C_{16}H_{10}$	202.26	394.2	129-00-0
PAH (Benzo[a]anthracene isomer)	5	-	-	-	-
Benzo[a]anthracene	5	$C_{18}H_{12}$	228.29	437.7	56-55-3
Crysene	5	$C_{18}H_{12}$	228.29	448.1	218-01-9
PAH (Crysene isomer)	5	-	-	-	-
Benzo[k]fluoranthene	5	$C_{20}H_{12}$	252.32	480.1	207-08-9
PAH (Benzo[k]fluoranthene isomer)	5	-	-	-	-
PAH (Benzo[a]pyrene)	5	-	-	-	-
Benzo[a]pyrene	5	$C_{20}H_{12}$	252.32	495.1	50-32-8
Perylene	5	$C_{20}H_{12}$	252.32	497.0	198-55-0

Data treatment

The tar yield of each individual compound in the gas mixture was then obtained by the expression:

$$Individual\ tar\ yield\left(\frac{mg\ tar}{g\ daf\ \ fuel}\right)=\frac{Tar\ concentration\left(\frac{mg}{l}\right)\bullet volume\ of\ \ solution\left(l\right)}{weight\ of\ daf\ \ fuel\left(g\right)} \qquad \text{(Aii-2)}$$

where: “tar concentration” is the concentration of the individual tar compound in the sample analyzed, “volume of solution” is the total volume of the sample where the tars were captured (0.5 l) and “weight of daf fuel” is the mass of fuel fed in a test discounting the mass of ash and water.

GC-MS analysis for primary tar compounds

Due to the large proportion of non-aromatic (or primary) tars at temperatures below 700°C, some tests were conducted to identify them and to determine whether it was possible to quantify them with the GC-MS device. However, different factors prevented the characterization of these tars using the GC-MS device. The main problem was the large amount of compounds that make the characterization of single compounds in SCAN mode difficult. Furthermore the samples containing primary tars rapidly deteriorate the GC column (dedicated to aromatic compounds) because of the irreversibly retention of these tars in the column. As a result of these difficulties, it was refused to use the GC-MS device for primary tar analysis.

Ai.3.4- Summarize of tar measurements

The Table Ai-2 summarizes the analytical measurements conducted to determine the composition of the tar mixtures.

Table Ai-2. Summary of analytical measurements conducted to tar samples in the present thesis

Analytical measurement	Procedure	Compounds measured
Gravimetric	Solvent evaporation of the solution where tars are captured	Compounds with a high molecular weight including primary compounds and PAH. Light compounds such as benzene and other monoaromatic tars (to a lesser extent) are mostly lost during evaporation
Elemental composition of the gravimetric tar	Elemental analysis of the gravimetric sample (without solvents)	This measurement determines the elemental composition (C, H, O, N, S) of the gravimetric tar mixture.
GC-MS analysis	Gas chromatography – Mass spectrometry of the solution where tars are captured	Aromatic compounds between one and seven condensed aromatic rings. This compounds belongs to the tertiary tars according with the classification presented in (Evans et al., 1998)

Appendix ii

Aromatic tar analysis

In this section the yields of the aromatic tars analyzed in Chapter 3 and 4 by GC-MS are presented. The results here presented are the average value of, at least, two different tests conducted in the same conditions. The yields are expressed in (mg/Kg daf fuel).

Table Aii-1. Yields of aromatic tars obtained in tests with homogeneous temperature in the reactor and in absence of steam.

Reactor temperature (°C)	**600**	**700**	**800**	**900**
Steam concentration (vol%)	**0**	**0**	**0**	**0**
Tar compound	**Tar yields (mg/Kg daf fuel)**			
Benzene	4452	25765	50397	77394
Tiophene	286	1118	1771	2300
Toluene	9690	17567	16783	8822
m-xylene (*p*-xylene)	692	1698	1259	239
Styrene	3185	6292	6420	4410
o-xylene	477	916	589	107
Phenol	2101	2740	2048	339
Benzonitrile	464	1754	3470	5242
Benzofuran	107	275	387	135
Indene	407	1792	2986	2731
m-cresol	3028	2444	772	232
Naphthalene	342	2120	5334	9859
2-methylnaphthalene	124	769	1041	592
1-methylnaphthalene	170	708	820	352
Biphenyl	84	211	402	575
2-ethenylnaphthalene	53	286	515	539
Acenaphthylene	62	353	1151	2430
Acenaphtene	31	36	49	37
Dibenzofuran	19	27	62	69
Fluorene	48	161	431	599
Phenantrene	68	427	1194	2369
Anthracene	32	106	395	701
4H-cyclopenta[def]phenanthrene	22	39	108	189
Fluoranthene	37	69	249	880
PAH (Fluoranthene isomer)	31	59	166	321
PAH (Pyrene isomer)	17	35	62	68
Pyrene	46	93	256	639
PAH (Benzo[a]anthracene isomer)	25	0	58	70
Benzo[a]anthracene	53	67	142	260
Crysene	65	122	197	248
PAH (Crysene isomer)	-	-	-	-
Benzo[k]fluoranthene	-	39	118	261
PAH (Benzo[k]fluoranthene isomer)	-	-	-	91
PAH (Benzo[a]pyrene)	-	-	93	211
Benzo[a]pyrene	-	15	121	299
Perylene	-	-	-	-

Table Aii-2. Yields of aromatic tars obtained in tests with homogeneous temperature in the reactor and with a 30 vol% of steam.

Reactor temperature (°C)	**600**	**700**	**800**	**900**
Steam concentration (vol%)	**30**	**30**	**30**	**30**
Tar compound	**Tar yields (mg/Kg daf fuel)**			
Benzene	4312	20375	50936	76064
Tiophene	302	650	2148	2421
Toluene	8273	17451	15646	6607
m-xylene (*p*-xylene)	643	1795	1128	169
Styrene	3003	5918	6531	3651
o-xylene	445	1000	530	63
Phenol	2395	2813	1353	243
Benzonitrile	577	1292	3918	5076
Benzofuran	113	252	397	100
Indene	404	1653	3163	2389
m-cresol	3052	2935	461	174
Naphthalene	357	1671	6124	11202
2-methylnaphthalene	138	720	985	474
1-methylnaphthalene	189	686	762	267
Biphenyl	95	216	383	606
2-ethenylnaphthalene	51	261	469	481
Acenaphthylene	53	314	1086	2422
Acenaphtene	29	46	43	35
Dibenzofuran	19	28	54	69
Fluorene	49	167	355	535
Phenantrene	70	359	1048	2321
Anthracene	29	92	348	658
4H-cyclopenta[def]phenanthrene	18	36	87	161
Fluoranthene	34	61	223	831
PAH (Fluoranthene isomer)	27	49	143	275
PAH (Pyrene isomer)	29	34	61	56
Pyrene	39	80	253	654
PAH (Benzo[a]anthracene isomer)	22	0	59	59
Benzo[a]anthracene	48	62	141	233
Crysene	59	112	194	237
PAH (Crysene isomer)	-	-	-	-
Benzo[k]fluoranthene	-	26	41	225
PAH (Benzo[k]fluoranthene isomer)	-	-	-	69
PAH (Benzo[a]pyrene)	-	-	33	158
Benzo[a]pyrene	-	13	137	244
Perylene	-	-	-	-

Table Aii-3. Yields of aromatic tars obtained in tests of formation of volatiles at various dense bed temperatures with freeboard temperature of 600°C.

Dense bed temperature (°C)	**500**	**600**	**700**	**800**
Freeboard temperature (°C)	**600**	**600**	**600**	**600**
Tar compound	**Tar yields (mg/Kg daf fuel)**			
Benzene	3025	4452	5601	13505
Tiophene	250	286	400	500
Toluene	9506	9690	11452	14118
m-xylene (*p*-xylene)	690	692	1199	1360
Styrene	3333	3185	4016	4750
o-xylene	380	477	697	753
Phenol	2276	2101	2688	2894
Benzonitrile	309	464	653	898
Benzofuran	80	107	182	225
Indene	356	407	762	1187
m-cresol	3610	3028	3768	3828
Naphthalene	331	342	653	1051
2-methylnaphthalene	113	124	381	468
1-methylnaphthalene	153	170	406	494
Biphenyl	83	84	189	198
2-ethenylnaphthalene	66	53	113	183
Acenaphthylene	103	62	122	207
Acenaphtene	29	31	41	58
Dibenzofuran	20	19	32	39
Fluorene	65	48	83	135
Phenantrene	137	68	142	224
Anthracene	51	32	48	68
4H-cyclopenta[def]phenanthrene	22	22	26	34
Fluoranthene	42	37	46	47
PAH (Fluoranthene isomer)	29	31	38	36
PAH (Pyrene isomer)	28	17	27	31
Pyrene	54	46	40	62
PAH (Benzo[a]anthracene isomer)	-	25	29	-
Benzo[a]anthracene	53	53	31	66
Crysene	62	65	45	94
PAH (Crysene isomer)	-	-	-	-
Benzo[k]fluoranthene	-	-	-	-
PAH (Benzo[k]fluoranthene isomer)	-	-	-	-
PAH (Benzo[a]pyrene)	-	-	-	-
Benzo[a]pyrene	-	-	-	-
Perylene	-	-	-	-

Table Aii-4. Yields of aromatic tars obtained in tests of secondary conversion of volatiles at various freeboard temperatures with dense bed temperature of 500°C.

Dense bed temperature (°C)	**500**	**500**	**500**
Freeboard temperature (°C)	**600**	**700**	**800**
Tar compound	**Tar yields (mg/Kg daf fuel)**		
Benzene	3025	11048	55104
Tiophene	250	511	1951
Toluene	9506	15256	21370
m-xylene (*p*-xylene)	690	1635	1578
Styrene	3333	5308	7697
o-xylene	380	981	728
Phenol	2276	2459	1937
Benzonitrile	309	900	2847
Benzofuran	80	250	366
Indene	356	1377	2736
m-cresol	3610	3254	1026
Naphthalene	331	1323	3714
2-methylnaphthalene	113	721	809
1-methylnaphthalene	153	628	674
Biphenyl	83	233	267
2-ethenylnaphthalene	66	230	450
Acenaphthylene	103	238	841
Acenaphtene	29	53	45
Dibenzofuran	20	34	42
Fluorene	65	133	326
Phenantrene	137	306	937
Anthracene	51	75	304
4H-cyclopenta[def]phenanthrene	22	31	89
Fluoranthene	42	59	194
PAH (Fluoranthene isomer)	29	47	140
PAH (Pyrene isomer)	28	30	57
Pyrene	54	66	168
PAH (Benzo[a]anthracene isomer)	0	30	36
Benzo[a]anthracene	53	38	142
Crysene	62	94	152
PAH (Crysene isomer)	-	-	-
Benzo[k]fluoranthene	-	50	89
PAH (Benzo[k]fluoranthene isomer)	-	49	47
PAH (Benzo[a]pyrene)	-	39	88
Benzo[a]pyrene	-	41	103
Perylene	-	-	-

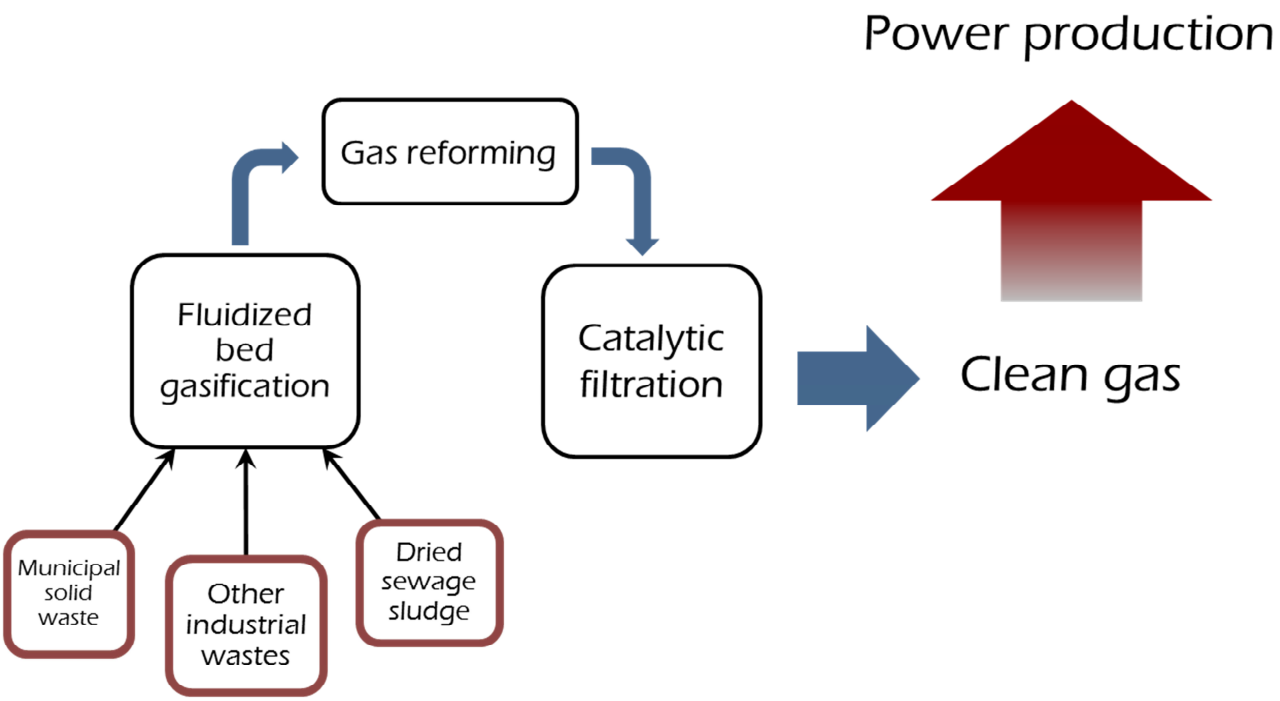
Table Aii-5. Yields of aromatic tars obtained in tests varying the DSS particle size with homogeneous temperature in the reactor of 800°C.

Particle size range (mm)	**1-1.4**	**2-2.8**	**4-5**
Reactor temperature (°C)	**800**	**800**	**800**
Tar compound	**Tar yields (mg/Kg daf fuel)**		
Benzene	31776	34338	33080
Tiophene	1309	1317	1249
Toluene	16193	17778	16433
m-xylene (*p*-xylene)	1262	1433	1259
Styrene	6066	6298	6047
o-xylene	609	678	606
Phenol	1778	1997	1775
Benzonitrile	3028	3194	3236
Benzofuran	372	389	383
Indene	2526	2615	2624
m-cresol	853	1028	751
Naphthalene	4965	4873	5320
2-methylnaphthalene	1362	1366	1383
1-methylnaphthalene	934	944	940
Biphenyl	490	487	497
2-ethenylnaphthalene	664	674	672
Acenaphthylene	1150	1157	1205
Acenaphtene	40	42	41
Dibenzofuran	67	76	69
Fluorene	437	461	461
Phenantrene	1244	1307	1335
Anthracene	370	385	404
4H-cyclopenta[def]phenanthrene	110	115	120
Fluoranthene	225	233	252
PAH (Fluoranthene isomer)	163	162	177
PAH (Pyrene isomer)	75	73	81
Pyrene	324	337	363
PAH (Benzo[a]anthracene isomer)	47	45	51
Benzo[a]anthracene	177	169	200
Crysene	262	243	294
PAH (Crysene isomer)	15	15	15
Benzo[k]fluoranthene	77	76	86
PAH (Benzo[k]fluoranthene isomer)	50	49	52
PAH (Benzo[a]pyrene)	52	51	56
Benzo[a]pyrene	93	88	104
Perylene	32	33	32

Table Aii-6. Yields of aromatic tars obtained in tests using wood pellets as fuel at different temperatures.

Fuel	**wood**	**wood**	**wood**
Dense bed temperature (°C)	**500**	**800**	**500**
Freeboard temperature (°C)	**600**	**600**	**800**
Tar compound	**Tar yields (mg/Kg daf fuel)**		
Benzene	1589	15535	30633
Tiophene	21	100	87
Toluene	1454	6983	8684
m-xylene (*p*-xylene)	324	995	1036
Styrene	396	2893	3627
o-xylene	151	505	440
Phenol	1821	5235	3769
Benzonitrile	105	346	491
Benzofuran	113	561	817
Indene	200	1633	3168
m-cresol	1757	3262	1563
Naphthalene	221	1184	2744
2-methylnaphthalene	64	455	625
1-methylnaphthalene	53	353	441
Biphenyl	40	133	172
2-ethenylnaphthalene	48	283	342
Acenaphthylene	65	310	665
Acenaphtene	22	68	61
Dibenzofuran	18	65	94
Fluorene	42	141	225
Phenantrene	93	227	492
Anthracene	38	83	158
4H-cyclopenta[def]phenanthrene	17	37	71
Fluoranthene	33	55	130
PAH (Fluoranthene isomer)	25	41	83
PAH (Pyrene isomer)	26	36	44
Pyrene	64	74	162
PAH (Benzo[a]anthracene isomer)	-	-	43
Benzo[a]anthracene	47	65	86
Crysene	52	61	69
PAH (Crysene isomer)	-	-	-
Benzo[k]fluoranthene	-	-	-
PAH (Benzo[k]fluoranthene isomer)	-	-	-
PAH (Benzo[a]pyrene)	-	-	-
Benzo[a]pyrene	-	-	-
Perylene	-	-	-

Departamento de Ingeniería Química y Ambiental
Escuela Superior de Ingenieros
Universidad de Sevilla
Abril 2013



UNIVERSIDAD D SEVILLA